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TRANSLITERATION

There is no ideal system of transliterating Russian; each has its advantages and disadvantages. For the translation of *Geokhimiya* we have chosen the system used by *Chemical Abstracts*, partly because of its wide acceptance by other journals and partly because of certain advantages in alphabetization of names. The principal differences between this system and others in common use are as follows:

Russian	Chem. Abs.	Others
X	kh	h
Ц	ts	tz
Щ	shch	sch
Ю	yu	iu
Я	ya	ia

THE KINETICS OF ARGON LIBERATION FROM MICROCLINE-PERTHITE

E. K. Gerling and I. M. Morozova

Laboratory of Precambrian Geology,
Academy of Sciences, USSR, Moscow

Abstract

The investigation was carried out over the temperature interval of 500° to
° with the aid of a mass-spectrometer. For the microcline-perthite used,
argon positions were ascertained, the isolations from which are connected
various values of the activation energy.
The activation energies of 15,000, 26,000 and 42,000 cal/g-atom of A charac-
ze the argon diffusion according to the disturbances of the crystal. Values of
activation energies of 99,000 and 130,000 cal/g-atom of A are connected with
ift of argon in the undisturbed lattice of the mineral. It has been shown with
aid of calculations that the argon amount in the first three positions of micro-
e-perthite equals 20% of the total content. A part of the easily isolated argon
be lost by the mineral, and therefore microcline is essentially unsuitable
age determination by the argon method.

Because of the abundance of potassium minerals and the relative
plicity of measuring A and K, the argon method of determining the
s of geologic formations has acquired prime importance. However,
reliability of the data obtained by this method depends on a number
actors and, first of all, on the retention of the radiogenic argon in
assium minerals. Important in this connection is the question of re-
ion of argon in feldspars and micas, since these minerals are wide-
sed in the determination of absolute ages. As early as 1953, Gerling
l. [1] showed that an age determined on microcline is always from
o 20% too low because of argon leakage. The substantial difference
rgon contents between micas and feldspars has also been mentioned
nany foreign authors [2, 3].
Finally, the $\lambda_K/\lambda_\beta = 0.085$ ratio obtained by Wasserburg and his as-
iates [4] by the geochemical method from specimens of feldspar is
oubtedly too low because of the loss of argon from the feldspars. In
darov's paper on "Retention of radiogenic argon in microclines" [5]
stated that the ages determined for the same rock on microcline
mica may differ by 10-15 to 70-75%. Thus, at present, there is no
ot of the different degree of retention of radiogenic argon by micas
feldspars, and it is timely to determine the causes for the differ-
and, if possible, to measure it. Many recent works have been de-
d to this problem. In his paper on the diffusion of argon from

micas and feldspars Reynolds [6] assumes that the leakage of argon from feldspars is entirely the result of volume diffusion. The value of the coefficient of diffusion, 10^{-19} cm^2/sec, found by him is sufficiently large to account for the 35% loss of argon from a grain of feldspar 1 cm in radius during $2000 \cdot 10^6$ years (the age of the feldspar). Without stopping to criticize this work in detail, we shall note that the German authors, Noddack and Zettler [7] and Gentner and Kley [8], in comparing the retentivity of argon by micas and feldspars take, apparently, the more correct position and ascribe the loss of argon from feldspars not to diffusion only, but mainly to alterations to which the feldspars are so susceptible.

In an attempt to determine the reliability of the data of the argon method for micas, we determined the value of the activation energy of the liberation of argon from these minerals [9]. The values we obtained, 85,000 cal/g-atom A for muscovite, 67,000 cal for phlogopite, and 57,000 cal for biotite, are very large and are comparable in magnitude to the bonding energy of the most stable chemical compounds. This showed convincingly why micas retain argon so well and lose it only when the crystal lattice is destroyed and the mineral as such ceases to exist. The activation energy or, as it is sometimes called, the heat of diffusion, which characterizes the energy state of the argon atoms and the crystal, and for which the movement of argon in the lattice of the mineral is possible, is the main criterion of retentivity of radiogenic argon. Therefore, by simply determining its value for the feldspars and comparing it with the value for the micas it is possible to explain the difference in the retention of argon by these minerals and to judge their suitability for age determinations by the argon method.

For our investigations we selected a specimen of "Panfilov Varak'" microcline. A thin section of this mineral exhibited a well developed microcline grid with albite veinlets; the degree of perthitization amounted to 7-10%. The method of determining heats of diffusion based on Grinberg's theory [10] regarding the general regularities of liberation of gases from metals on heating was described by us in a previous work. It should be recalled that to compute the heat of diffusion, it is necessary to discover the nature of the liberation of argon at different temperatures and to observe the dependence of its separation on time. To determine this dependence, the gases escaping from the mineral during the process of heating were passed, at definite intervals of time, into absorbers with activated charcoal. After the separation, the gases were purified in the usual manner, and the final amount of argon was measured in a McLeod gauge. This method is very time-consuming and requires relatively large amounts of material. In order to speed up the work of determining the heat of diffusion during the liberation of argon from potassium minerals, it was necessary to devise a more efficient procedure. We decided to use a mass spectrometer for our investigation of the kinetics of argon liberation from minerals. It is known that such a procedure is quite possible [11], if a molecular flow of gas into the ionization chamber through the leak is created. Only if this is done

l the gases in the mixture enter into the mass spectrometer inde-
ndently of each other and the intensity of the peak of the required gas
l change with its partial pressure, i.e., the relation $I_M = \alpha_M P_M$. In
experiment the molecular flow of gas liberated from the mineral
ted to a definite temperature entered the ionization chamber of the
ss spectrometer adjusted for A^{40}. The measurements of the changes
he intensity of the peak with time began at the moment of attainment

he quasi-equilibrium state for which $\dfrac{dQ}{dt} = SP_A$, where $\dfrac{dQ}{dt}$ is the

ocity of liberation of gas from the mineral, S is the pumping rate and
the partial pressure of argon.

The experimental data obtained by the old, tried method are shown in
ure 1 a. The curves representing the kinetics of liberation of argon
asured by the mass spectrometer are given in Figures 1 b, and 2 e.
An examination of Figure 1 a, in which the amounts of liberated ar-
are plotted on the ordinates and the time of liberation on the abscis-
, shows that, in all cases, the curves consist of at least two straight
ments. This indicates that argon in microcline is present in several
itions, each of which is characterized by a definite heat of diffusion.
straight segments in the diagrams are due to simultaneous libera-
of argon from two different positions. That position of argon from
ch its liberation requires the least activation energy, we shall call
first position. As the temperature rises the diffusion of argon from
II, III etc. positions is invariably related to increased activation en-
y. If the processes of liberation of argon from different positions
regarded as independent of each other, then it is always possible to
luate the effect of each successive process on the amount of argon
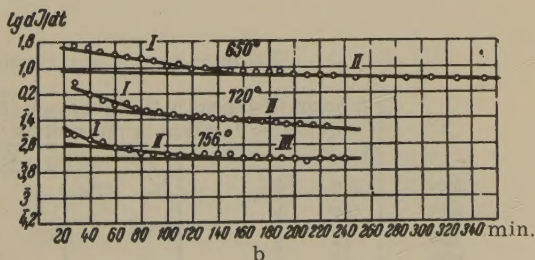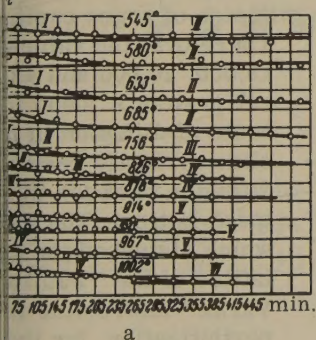
1. Curves for the kinetic emission of argon from microcline-perthite.
$\lg K_{II}^{633°} = \bar{3}.09$; $\lg K_{II}^{685°} = \bar{3}.42$; $\lg K_{III}^{756°} = \bar{3}.12$; $\lg K_{IV}^{878°} = \bar{4}.82$; $\lg K_{V}^{332°} = \bar{4}.47$;
$\lg K_{V}^{967°} = 4.95$. b—$\lg K_{II}^{650°} = \bar{3}.24$; $\lg K_{III}^{720°} = \bar{3}.62$; $\lg K_{III}^{756°} = \bar{3}.18$

liberated by diffusion from the preceding position in the mineral and to draw lines representing any given process. Thus, in order to separate curve II of the process at 765° C in Figure 1, a, the segment of the line of the third process is continued to the intersection with the ordinate and from the points belonging to the second process, the amount of argon liberated by diffusion from the third position is subtracted. The corrected straight lines which characterize the liberation of argon from its various positions are shown in Figure 2, a, b, c, d and e. Using the experimental values for K, it is possible to compute the amount of argon, M_1, which has not yet been liberated from certain positions in the mineral at a certain moment of time, t, according to the formula:

$$N_I = \frac{N_2}{e^{Kt} - 1},$$

where N_2 is the total amount of argon liberated from the mineral in the time t. Adding the amount of argon N_1 to that liberated during the experiment, it is possible to determine the total amount of argon in each position in the mineral. The results of such computations are given in the table.

To make a direct computation of the values of activation energy of the liberation of argon from microcline, logK is plotted on the ordinate $\frac{1}{T} \cdot 10^6$ on the abscissae (Fig. 3). The heats of diffusion are determinable from the slopes of the straight lines so obtained. They are: 15,000 cal/g-atom A for position I, 26,000 cal for position II, 42,000 cal for position III, 99,000 cal for position IV and 130,000 cal for position V.

It is interesting to note that Reynolds [12], in his study of glass containing K—CaO—SiO$_2$, also obtained the value of 42,000 cal/g-atom A. It is known that in the process of formation of glass the SiO$_2$ crystal lattice expands a little and this makes the diffusion of argon easier. Therefore, the values of 15,000, 26,000 and 42,000 cal/g-atom A found for the heats of diffusion in microcline evidently relate to the diffusion of argon in an altered lattice. The process which disturbed the crystal lattice of the "Panfilov Varak" microcline was perthitization, for the exsolution of the solid solution of potash and soda feldspars increases the internal surface of the lattice and the diffusion of argon made easier. The amount

Table

t°	Amount of argon, in %, occupying the following location in microcline				
	I	II	III	IV	V
633	17				
685	17				
756	15		7		
806	17				
826		3			
878		5			
914				9	
932				6	
967			3		65
Average value	16	5	6		65
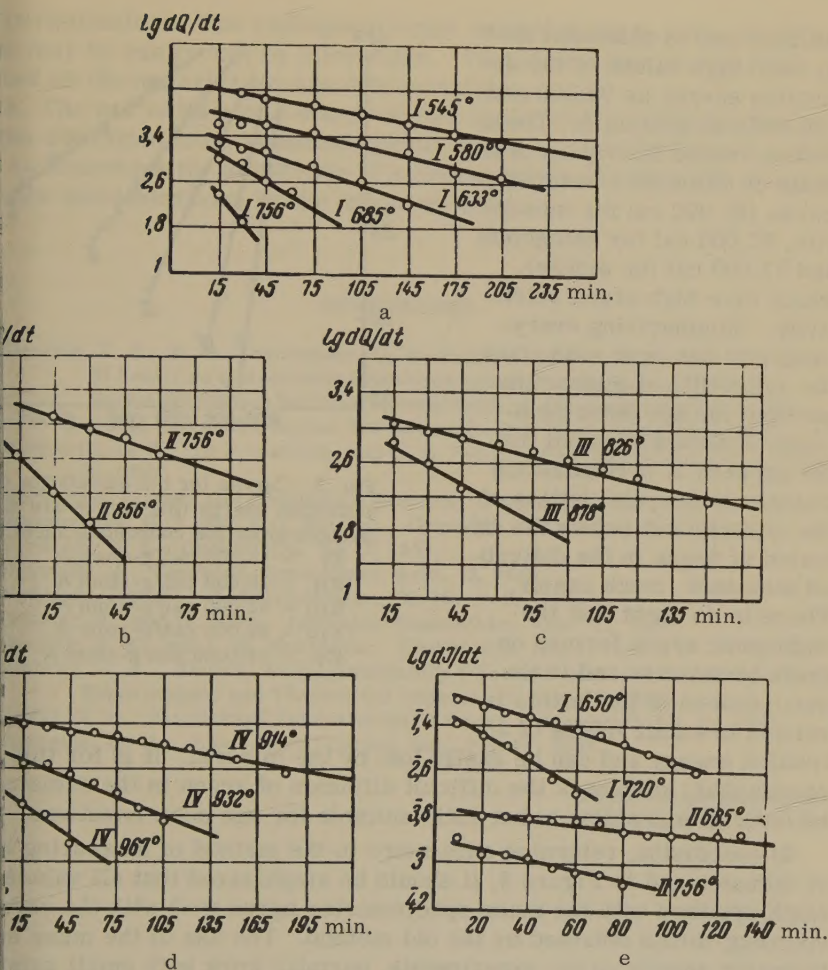
. Curves for the kinetic emission of argon from microcline-perthite, with
ction calculations.

$lgK_I^{545°} = \bar{3}.66;$ $lgK_I^{580°} = \bar{3}.85;$ $lgK_I^{633°} = \bar{3}.97;$ $lgK_I^{685°} = \bar{2}.18;$ $lgK_I^{756°} = \bar{2}.55.$
$K_{II}^{756°} = \bar{3}.97;$ $lgK_{II}^{826°} = \bar{2}.23.$ $c - lgK_{III}^{826°} = \bar{3}.85;$ $lgK_{III}^{878°} = \bar{2}.16.$ $d - lgK_{IV}^{878°} =$
$lgK_{IV}^{932°} = \bar{3}.99;$ $lgK_{IV}^{967°} = \bar{2}.31.$ $e - lgK_I^{650°} = \bar{2}.06;$ $lgK_I^{720°} = \bar{2}.36;$ $lgK_{II}^{685°} =$
$\bar{3}.47;$ $lgK_{II}^{756°} = \bar{3}.96.$

gon easily liberated from microcline, as can be seen from the
is 20%. For micas this amount is small and amounts to 2—3% of
tal argon content.
e diffusion of argon in an undisturbed lattice of microcline is very

difficult and is characterized by such high values of the activation energy as 99,000 and 130,000 cal/g-atom A. These values exceed the values of the heats of diffusion measured in micas (85,000 cal for muscovite, 67,000 cal for phlogopite and 57,000 cal for biotite), which have high argon retentivity. Summarizing everything that has been said about the suitability of microcline perthite for age determinations, it should be noted that the process of perthitization changes the crystal lattice of the mineral and makes the diffusion of argon in the disturbed structure, much easier. There is no doubt that the radiogenic argon formed on grain boundaries and in the inner spaces of the lattice is related to small values of activation energy and can be easily lost by the mineral. It is for this reason that, in spite of the difficult diffusion of argon in the undisturbed lattice, microcline is but little suitable for age determinations.

Fig. 3. Curves for the calculation of activation energy (the curves are distributed along the coordinate axes).

E_I = 15,000 cal/g-atom A
E_{II} = 26,000 cal/g-atom A
E_{III} = 42,000 cal/g-atom A
E_{IV} = 99,000 cal/g-atom A
E_V = 130,000 cal/g-atom A

In conclusion, returning once more to the method of measuring heats of diffusion and to Figure 3, it should be emphasized that all values of LogK obtained with the mass spectrometer agree well with the corresponding values obtained by the old method. The use of the mass spectrometer speeds up the experiments, permits work with small samples of minerals and makes it possible to determine heats of diffusion of various potassium minerals, i.e. to discover their suitability for age determinations by the argon method.

The preceding discussion can be summarized as follows:

1. The kinetics of argon liberation from microcline were studied in the interval from 500 to 1000° C. For the five positions of argon discovered in microcline the following heats of diffusion were obtained:

15,000	cal/g-atom	A	for position	I
26,000	"	"	"	II
42,000	"	"	"	III
99,000	"	"	"	IV
130,000	"	"	"	V

2. The activation energies of 15,000, 26,000 and 42,000 cal/g-atom A, characterize the diffusion of argon in the mineral lattice disturbed

perthitization. The radiogenic argon related to these heats of diffu-
sion may be easily lost by microcline. This makes microcline little
suited as the material for age determinations.

3. The use of the mass spectrometer in the study of the kinetics of
argon liberation from minerals speeds up the work and makes it possi-
ble to determine the suitability of a great variety of potassium minerals
for age determinations by the argon method.

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GEOCHRONOLOGICAL SUBDIVISION OF THE PRECAMBRIAN OF THE UKRAINE

L. V. Komlev

V. G. Khlopin Radium Institute,
Academy of Sciences USSR, Leningrad

Abstract

Numerous age data obtained with the aid of argon and lead-isotope methods for Precambrian rocks of the Ukraine have been critically examined. A scheme for the geochronological subdivision of the Precambrian of the Ukraine is given in which 5 magmatic complexes participate. The chief mass of Ukraine granite has been formed within the narrow time interval of 1550-2100 million years, with a sharply marked culmination of magmatism in the interval of 1900-2100 million years. The most ancient migmatite and gneiss formations have lasted in the form of separate blocks, for which it is expedient to preserve the name Katarkhea. A progressing geochemical differentiation of magmas with an enrichment in radioactive elements—potassium, uranium, and thorium—has been established in derivatives of younger cycles. A typical change of accessory minerals from allanite to monazite and thorite is observed. All this bears witness to a definite trend in the geochemical evolution of the crust of the earth in the Ukraine Precambrian.

The Precambrian crystalline massif of the Ukraine is one of the first large geological regions of the Soviet Union on which, during the past five years, a number of research groups developing methods of absolute geochronology have concentrated their attention. Because of the favorable geochemical characteristics of the Ukrainian Precambrian magmatic complexes revealed by the preliminary regional geochemical investigations, it developed that systematic age determinations could be made not only on the rock-forming minerals by the argon method, but also by wide application of the lead isotope method to the radioactive accessory minerals separated from the rocks, mainly to monazite.

The scale of the completed investigations may be illustrated by the following figures, which do not, by any means, include all of the relevant work. There are more than 250 age determinations made by the argon method on micas, feldspars, and rocks. In this paper we use only the most reliable data obtained from 140 samples of micas. Half of these data were obtained by us.

About 100 monazites separated from the main types of granitoids and associated pegmatites have been dated by the lead isotope method. Sixty-six determinations were made by us. Besides this, we used other radioactive minerals for age determinations, namely, allanite, thorite, uraninite, brannerite, zircon, and sphene.

large number of age determinations were made in the V. I. Ver-
tii Institute of Geochemistry and Analytical Chemistry, Academy
iences USSR, by A. P. Vinogradov, using the argon and lead meth-
Very valuable determinations by the argon method were made by
Gerling in the Laboratory of Precambrian Geology, Academy of
ces USSR, on our and A. P. Nikolskii's material and by N. I. Po-
a at the All-Union Geological Institute on Yu. Ir. Polovinkina's
rial. Systematic age studies have been organized also by N. I. Se-
nko, E. S. Burkser, and M. N. Ivantishin at the Geological Institute
Ukrainian Academy of Sciences.

fortunately it was necessary to exclude from consideration all the
obtained by the argon method from feldspars and rocks because
are, as a rule, too low as compared with the ages determined on
s and those obtained by the lead method.

here is no doubt that this detailed study by two geochronological
ods mutually controlling each other gives the Precambrian of the
ine primary rank in the world so far as regional geochronological
tigations are concerned. In spite of the fact that many of the in-
gations are still incomplete and the collection of data on the
inian Precambrian will continue, it is timely to present certain
aries.

he first attempt to use the geochronological data as a basis for the
igraphic subdivision of the Ukrainian Precambrian was made by
nenko and Burkser in 1955 in their report to the Fourth Session of
ommittee for the Determination of the Absolute Age of Geologic
ations at Moscow [1]. This attempt was premature and could not
substantial results because of the uncritical approach of the au-
to the interpretation of the very contradictory age data obtained
e argon and lead methods which were available at that time.

1956, at the Fifth Session, in Tbilisi, I presented a generalized
ing scheme of geochronological subdivision of the Ukrainian Pre-
rian [2]. In the same year, Vinogradov [3], in his summary report
Geological Congress in Mexico, defined age intervals for a group
agmatic complexes of the Ukraine using his own and our data.
hese generalizations played a positive role, for they quite definitely
lished the suggested age groups and revealed a number of serious
adictions both in the interpretation of the age data and in the esti-
s of the ages of individual important stages in the development of
krainian crystalline shield during the Precambrian.

he publication of the most recent work by Semenenko [4], an ex-
tory note to the newly compiled structural-petrographic map of
krainian crystalline massif, must be especially noted.

this brief note, the author, who is one of the initiators of the broad
cation of the data of absolute geochronology to the study of the
nian Precambrian, gives a geochronological scheme which, as will
en, differs substantially from the one proposed by us.

e main difference between the two schemes is in the unsubstanti-
from our point of view, tendency in Semenenko's scheme towards

underestimating the age of a number of geological complexes of the Ukraine and towards assigning to the entire enormous segment of Precambrian time of $2\frac{1}{2}$ billion years a very limited number of tectonic-magmatic complexes (five).

The complexity of the problem lies in the fact that the existing geological concepts about the main stages of development of the Ukrainian Precambrian are indefinite, not only in detail, but even in their main premises, and require much additional profound study on the basis of the most recent data.

Several variants of the geological concepts of the history of the formation and development of the Ukrainian crystalline massif have been worked out. These concepts are, as a rule, the results of many years of work and of generalization from a large number of disconnected geological data [5, 6]. To a considerable extent they represent a critical reworking of old ideas which always have as their basis the primitive fourfold subdivision of the Precambrian into Lower and Upper Archean and Proterozoic without any consideration of the scale of geologic time.

It is quite natural to expect under these circumstances that the data of absolute geochronology will be accommodated to the already existing schemes of structural and stratigraphic subdivisions. This led Semenenko to an erroneous interpretation of the meaning of the argon ages obtained on feldspars and rock samples, which are usually too low. This explains also the incorporation into his scheme of obviously incorrect, very low age values obtained by the lead method on materials which require further careful investigation.

In working out our geochronological scheme, we accepted only the age data which have been subjected to strict critical selection from the point of view of methodological requirements and the requirements of the necessary geological documentation. We were fortunate to have at our disposal abundant, very carefully selected mineralogical material from practically all the geological complexes of the Ukrainian Precambrian, and for most of them obtained ages in our laboratory by independent argon and lead methods [2, 7-17].

In Table 1 we present the generalized age data for the main groups of Precambrian rocks of the Ukraine. Table 2 presents a geochronological subdivision of the Precambrian Ukrainian crystalline shield, which is a further development of our working scheme of 1955 presented to the Fifth Session of the Committee in Tbilisi and of the material of Vinogradov's report [18].

All the argon ages have been recalculated by us on the basis of the new decay constant of K^{40} ($\lambda_K = 0.557 \cdot 10^{-10}$ years; $\lambda_B = 4.72 \cdot 10^{-10}$ years) determined by the geochemical method [19].

Let us examine the data of Table 1 and the geochronological scheme proposed by us. The argon and lead ages given in the appropriate columns are generalized from all of the ages available for each group of rocks. Only the most reliable lead ages were used. When age determinations gave a considerable scatter, they were either discarded completely or an age interval was established, which includes the true age by a critical examination of the data.

Table 1. Age Data for the Precambrian Rocks of the Ukrainian Shield,
by the Argon and Lead-Isotope Method

Rock group	Age, in mil. of years	
	Argon method	Lead method
v area alkaline complex	1500	(1850)
anskii, antonovskii granites	1560	—
aplite granite of Novo-Ukrainka, Novo-Arkhangelska		1650-1750
ostensk, Novo-Mirgorodskii rapakiwi granite	1750	1600-1750
ovyansk, verblyuzhinskii granite	1700-1800	1600-1800
ovsk granite	1800	—
matites from the Azov-Area migmatites	1800	1700-2000
terinovsk and Kamennye Mogily granite	1900	—
o-Ukrainka trachyte granite	1930	1900
omir granite	1900	—
ostyshevsk granite	2000	—
uslavsk granite	1950	—
ovograd granite	1960	1975
rinetsk granite	1950	1960
tvovod R. granites	—	1970
rnockite and red aplite granite from Podoliie	—	1950
tsevsk granite	2000	—
vomaisk granite (Krivorozhe)	2000	—
oi Rog series metamorphic schists	1900-2000	2000
urinsk granite	2000	—
nsk granite	2100	—
o-Danilovsk granite	2000	2100
otkansk granite	2100	—
River granodiorites (sobites)	—	2100
rebishensk red aplite granite	—	2100
o-Ukrainka Monzonite	—	2100
dnovo-Berdichev granite	—	2100
sagan plagiogranite	2100	—
menchug granodiorite	2070	—
nigorod plagiogranite	2100	—
amorphism of the Teterevo-Bug Volyna neiss series	2000-2100	—
amorphism of the Krivoy Rog series	2000-2100	—
nite pegmatites in the Dnepr-area nigmatites		
Korbino	2280	2350
Repikhovo	2130	2600
Reevo	2360	2660
Podstepnoe	—	2670
raya Surar (Yamburg Karer) ancient ranodiorite	2900	—

Table 2. Diagram for the Geochronological Classification of the
Precambrian Magmatic Rocks of the Ukrainian Shield

Magmatic complex	Granite types	Age, mil. years
V. Umansk-Azov area	a) Umansk, antonovsk granite b) Azov area alkaline complex	1550-1750
IV. Korostensk-Bokovyansk-Tokovsk	a) Korostensk and Korsun-Novo-Mirgorod rapakivi granites, gabbro-labradorites, monzonites b) Bokovyansk-verblyuzhin charnockite granite c) Tokovsk granite d) Ekaterinovsk granite	1700-1800
III. Kirovograd-Zhitomir	a) Kirovograd, Korostyshev Zhitomir, Boguslavsk, Bobrinetsk, Mertvovod, Pervomaisk, Yantsevsk b) Novo-Ukrainka trachyte granite c) Podolie charnockite granite	1900-2000
II. Podoisk-Krivoi Rog	a) Dolinsk, Novo-Danilovsk, Domotkansk, Demurinsk b) Chudnovo-Berdichevsk c) Sob R. granodiorites (sobites) d) Saksagan, Kremenchug, Evenigorodsk plagiogranites	2000-2100
I. Dnepr	a) Ancient Dnepr-area migmatite blocks b) Mokraya Sura R. granodiorites	2300-2900

This was done also for the cases of scatter of age data obtained for different samples of the same rock. The ages obtained by two independent methods or representing an average age of a group of consistent samples are printed in italics. They are the most reliable within the limits of error (±3%).

To the group of oldest igneous rocks of the Ukrainian Precambrian belong the granodiorites of the Mokraya Sura River and the quartz feldspar biotite pegmatites that cut them. According to the data obtained by the argon method from the amphibole-biotite fraction separated from the granodiorites and from the phlogopite of the Yamburg quarry pegmatites, the age of these rocks, confirmed by control analyses, is 2,900 million years. At present this is the greatest argon age determined in the Ukraine.

Somewhat lower ages have been obtained for a series of allanite pegmatites occurring in the migmatites of the Dnepr region. These are pegmatites on the Saksagen and Ingulets rivers studied by Vinogradov and Tugarin [20]. We have obtained an equally high age of 2,350—2,670

million years for the allanite pegmatites of the Korbinsk quarry on the Dnepr and of the Staryi Podstepenskii quarry on the Bazavluk River [ ]. The lead isotope ages are confirmed by the very high values of argon ages determined for phlogopite.

Evidently we deal here with individual relict blocks in the oldest migmatites. It is convenient to group all these very old igneous rocks of the Ukrainian Precambrian under the name of the *Dnepr* magmatic complex.

It is evident that the gneisses, which were changed into migmatites and are cut by the oldest granodiorite intrusives, are still older. Unfortunately there is no direct way of determining the age of these gneisses, and it is not likely that accurate ages can ever be obtained for them. For the metamorphic rocks of the gneiss sequence, wide-spread in the form of separate blocks among the migmatites of the Ukrainian Precambrian, it is possible to obtain only the upper limit of the time of metamorphism. In a series of determinations of the time of metamorphism of the gneiss sequence of Krivoi Rog and Volyniya Ger- [21], the author [10] obtained ages of 2,000—2,100 million years. Inasmuch as in metamorphic rocks only the time of formation of the crystal lattices of the rock-forming potassium minerals (microcline, biotite, and muscovite) can be determined, the true age of the volcanic and sedimentary parent rocks of the gneisses must obviously be greater than 2,000—2,100 million years.

According to Goldich, Baadsgaard, and Nier [22], all of the meta-morphic Precambrian rocks of the Thompson formation (Minnesota), which include shales and phyllites, schists and gneisses, gave consist-ent argon ages. This indicates that the formation, in the course of pro-gressive metamorphism, of fine-grained sericitic material creates fa-vorable conditions for dating by retaining radiogenic argon.

Considering the complex composition of the gneisses and the great variety of the conditions of metamorphism in different structural zones, the effect of the later igneous masses and of metasomatic processes, substantial age differences must be expected for individual metamor-phosed areas and formations. The possibility of subdivision of the gneisses into individual formations is accepted now by all geologists and this indicates that the gneisses record a very long period of time.

The biotite-plagioclase and pyroxene-plagioclase gneisses and some amphibolites, are, according to Polovinkina [23], the oldest rocks of the Ukrainian crystalline shield. In light of the new data, it may be expect-ed that very old formations will be found among the relict blocks of the gneiss sequence with ages of the order of 2,500—3,500 million years, as suggested by the ages obtained for the allanite pegmatites and gra-nodiorites of the Dnepr region which are injected and intruded into the gneisses.

The age of 2,000—2,100 million years assumed by us for the gneiss-es has been obtained for individual areas only, and represents the age of the widespread intrusives, mainly granodiorites and plagiogranites which had the strongest metamorphic effect on the oldest volcanic and

sedimentary formations. The age of this group of granitoids, according to our [12] and Gerling's [24] data, is 2,000—2,100 million years. To this group belong, first of all, the Saksagan, Kremenchug and Zvenigorodka granodiorites and plagiogranites, all of which are of the same age (2,100 million years), in spite of the opinion of some geologists.

Synchronous with these rocks (within ± 50 million years, the limit of accuracy of the methods) are the Chudnovo-Berdichev granites, the granodiorites of the Sob River (sobites), and the associated red aplitic granites of the Pogrebishchensk, Ilintsev, and other regions of distribution of sobites and the Chudnovo-Berdichev granites. Their ages have been determined very reliably on monazite by the lead isotope method.

The manifestations of certain later regional processes in the Chudnovo-Berdichev and charnockite formations deserve especial notice, for they are responsible for the very low argon ages obtained both on the micas separated from the granites and from the associated pegmatites. This problem requires further study [14].

To the same age group belong the Domotkansk and Novo-Danilovsk granites, which were formerly believed to be much younger, and the Dolinsk and Demurinsk granites. The Novo-Danilovsk granites have been very reliably dated by the monazite and micas separated from the pegmatites and the granite itself [12].

The large group of granites, usually considered as a part of the Kirovograd or Kirovograd-Zhitomir magmatic complex, is characterized by argon and lead ages ranging from 1,900 to 2,000 million years. This group includes the gray porphyritic Kirovograd and Bobrinets granite, the granites of the Mertvovod and Arbuzinka rivers, Pervomaisk, Demurinsk, Boguslavsk, and Korostyshev granites and the medium-grained Zhitomir and Yantsev granites.

To the same age group belong the charnockite hybrid granites of Podoliya and the red aplitic granites associated with them. It is believed by many authors that the Podolian charnockites, like the Chudnovo-Berdichev granites, belong to the Kirovograd magmatic cycle.

We have established the near contemporaneity of the Kirovograd granites and the red gneissoid granites of the Novo Ukrainka region that crop out on the Cherny and Pletenyi Tashlyk rivers and on the Sugoklei River. The age of these granites, 1,900—2,100 million years, has been very reliably determined on accessory monazite and on mica.

Thus, it may be said that the age of the Kirovograd-Zhitomir complex has been very firmly established as 1,900—2,000 million years, if the plagiogranites and some other similar granites are included in the complex, as 1,900—2,100 million years.

We should like to discuss in some detail a very controversial problem of the Ukrainian Precambrian, the relationship between the granites and the Krivoi Rog schists. The geologists' opinion is divided on this subject, and geological evidence is evidently insufficient to solve the problem.

Polovinkina [5, 23, 25] considers that the Saksagan plagiogranites

the Kirovograd granites antedate the Krivoi Rog schists. The very
intensive metamorphism and migmatization of the gneisses was caused
by these intrusions, but the rocks of the Krivoi Rog series exhibit the
effect of these processes to a much smaller degree.

In Polovinkina's opinion, the crosscutting relationship of the am-
phibolites underlying the Krivoi Rog series with respect to the Saksagan
plagiogranites has been completely established. According to her, the
arkosic horizon of the lower part of the Krivoi Rog series lies on the
eroded surface of the plagiogranites.

A confirmation of these views is Goroshnikov's [26] discovery, in
the conglomerates of the arkosic horizon of the lower section of the
Krivoi Rog series, of large pebbles of gray medium-grained granites
corresponding in composition to the plagiogranites and normal granites.
Zaevtsev [27] also believes that the Saksagan plagiogranites are older
than the Krivoi Rog series, but considers the Kirovograd granites as
post-Krivoi Rog.

An entirely different point of view on the relationship of the granites
to the Krivoy Rog metamorphics is held by other geologists. Accord-
ing to Semenenko [28], apophyses of gray granite penetrate the rocks of
the Krivoi Rog series. He found injections of gray granite in the upper
portion of the series (near the village of Petrovo). Xenoliths of the fer-
ruginous rocks of the Krivoi Rog series have been found in the migma-
tites on the Ingulets River. Thus, the granites of the Krivoi Rog region
are obviously younger than the metamorphic rocks of the Krivoi Rog
series.

Kotlyar [29] gives the following magmatic sequence in the Krivoi Rog
region:

1. Pre-Krivoi Rog extrusives and ultrabasic and basic intrusives of
   the greenstone complex.
2. Post-Krivoi Rog ultrabasic rocks.
3. Post-Krivoi Rog Saksagan plagiogranites.
4. Post-Krivoi Rog gray granites of the Kirovograd type.
5. Pink microcline granites of late post-Krivoi Rog age.
6. Diabase dikes of post-Krivoi Rog age.

Nikolskii [30] also believes that the post-Krivoi Rog age has been
established, not only for the gray Kirovograd granites but for the
Saksagan plagiogranites, which, according to his observations, cut the
rocks of the greenstone sequence and the arkosic horizon of the lower
part of the Krivoi Rog series.

As for the Saksagan plagiogranites, some geologists consider them a
part of the Kirovograd complex and regard the latter as either older or
younger than the Krivoi Rog series. Others separate gray granites and
plagiogranites into a pre-Krivoi Rog and post-Krivoi Rog groups. Thus,
the geologists' views on this subject are very contradictory.

Let us turn now to the absolute age data, which even now can throw
some light on the problem.

The age of metamorphism of the schists in the middle section of the

Krivoi Rog series was determined by Gerling [21] on micas especially selected by Nikolskii as 1,900—2,000 million years. The lead isotope ages determined by the author and A. I. Tugarin for some mineralized areas in the middle part of the series agree with Gerling's data.

The age of metamorphism of the schists of the middle section of the series may be considered as reliably established and not accidentally coinciding with the age of the main mass of the gray Kirovograd complex. Only in some areas of intensive effect of the younger red granites can later manifestations of metamorphism be expected. Semenenko's [4] tendency to assign low ages of 1,820 to 1,950 million years (after recalculation to the new constants) to the Krivoi Rog series is in obvious conflict with these data.

If the long process of accumulation of the sediments of the Krivoi Rog series previous to metamorphism is taken into consideration, the actual age of the rocks must exceed the age of metamorphism; i.e., it must be greater than 1,900—2,000 million years. Evidently the maximum age of these rocks cannot be greater than 2,100 million years, the age of the Saksagan plagiogranites, assuming that the information about the discovery of plagiogranite pebbles in the basal beds of the arkosic horizon is correct.

In the author's opinion, it is more correct to divide the gray granite into two complexes, the *earlier one*, pre-Krivoi Rog and essentially plagiogranite and granodiorite complex, and a *later one*, essentially granitic post-Krivoi Rog complex of the middle stages of development of the mobile zone to which most of the normal granites must be referred. The author proposes that the earlier complex, the second to be formed and composed of granitoids ranging from 2,000 to 2,100 million years in age, be called the *Podol'sk-Krivoi Rog* complex in order to emphasize the important role played in it by the granitoids of the Krivoi Rog region, the Chudnovo-Berdichev granites and the sobites of Podolya. For the later, third complex, with the age of granitoids ranging between 1,900 and 2,000 million years, the name *Kirovograd-Zhitomir* complex may well be retained. It is obviously post-Krivoi Rog.

The time of accumulation of the sediments of the Krivoi Rog series thus falls into a relatively small interval of geologic time, of the order of 100 million years, which under the conditions of geosynclinal subsidence is an ample time for the accumulation of thick sedimentary and volcanic deposits of all three sections of the series.

A younger group is formed by the Tokovsk, Bokovyansk, Korostens, Korsun-Novo Mirgorod, and a number of other, mainly red and rapaki granites. The ages determined for these granites range from 1,650 to 1,900 million years, with a marked predominance of the most reliable ages in the interval between 1,700 and 1,800 million years. The absolute age determinations provide a good basis for grouping younger granites into a fourth, or Korostensk-Bokovyansk-Tokovsk magmatic complex. This complex is characterized by the predominance of siliceous potassium granites, commonly of the alaskite type.

The absolute ages are in complete agreement with the opinion of

ne geologists, especially of Polovinkina [23], that petrologically
se granites belong to a single magmatic complex. Evidently the
terinovskii and Kamennaya Mogila granites of the Azov region
uld also be referred to this group.

The youngest, fifth, magmatic complex, according to the argon ages,
ludes the Uman and Antonov granites, for which there are two series
ompletely consistent age determinations made on micas at the Ra-
n Institute [15] by the writer and in the All-Union Geological Insti-
by Polevaya [31]. The age of this complex, determined as 1,560
ion years, requires checking by the lead method.

For the granites and syenites of the alkalic complex of the Azov re-
, Gerling obtained the age of 1,550 million years, using micas.
s determination requires further refinement, but apparently these
ks are contemporaneous with the Uman granites.

Lower ages in the Ukrainian Precambrian have so far been deter-
ed with certainty for the dike complex and for certain products of
eralization, both phenomena being probably related to fracturing of
rigid massif caused by the later tectonic phases and resulting mag-
c and hydrothermal activity.

The author believes that in the geochronological scheme proposed by
enenko, Ivantishin, and Burkser [4], the ages given for the later
matic cycles must be revised and increased.

n conclusion the characteristic features of the development of mag-
sm on the Ukrainian Precambrian shield should be pointed out. The
n mass of granites and their derivatives was formed during a rela-
y short interval of geologic time between 1,550 and 2,100 million
s ago, with a sharp increase in igneous activity between 1,900 and
million years ago.

eparate fragments of geologic history are traceable as far back as
million years into the depths of time and require further study.
possible that we should return to the concept of Katarchean time
eplace in the stratigraphic column the oldest group of the Dnepr
atites of Luchitskii [32].

he geochemical evolution of magmatism from the predominance of
and calc-alkalic granitoids, plagiogranites, and granodiorites in
arlier magmatic complexes to normal granites of the Kirovograd-
mir complex and further to leucocratic potash granites of the
ger complexes is clearly defined. This was noticed by the author
50 [7] and later confirmed by Yurk [33].

e have established that there is a regular change in the radioactiv-
igneous rocks from very low values in the early plagiogranite-
diorite complexes to very high values in the acid granites of the
complexes. We have observed, at the same time, a characteristic
ge in radioactive accessory minerals from allanite to monazite and
e. These facts are indicative of a definite geochemical evolution
earth's crust in the region of the Ukraine during the Precambrian.

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NEUTRON EMISSION FROM MINERALS AND THE ORIGIN OF Ne²¹ IN THE EARTH'S ATMOSPHERE

L. L. Kashkarov and V. V. Cherdyntsev

S. M. Kirov Kazakh State University, Alma Ata

Abstract

The neutron radiation of radioactive minerals has been examined. For fer... thorites the average neutron yield is 0.9 ± 0.2 neutrons per 10^6 α-particles an... for uranium minerals 0.39 ± 0.03 neutrons per 10^6 α-particles. It has been shown that about 40% of neutrons in the radiation of uranium minerals are neu... trons of a spontaneous fission.

The chief reaction of the artificial transformation leading to neutron forma... is the O^{18} (αn) Ne^{21}-reaction. The neutron yield at the expense of it is about 0... per 10^6 of α-particles both for the thorium and the uranium family. It has be... shown that no less than a quarter of Ne^{21} of the earth atmosphere is connected... with the formation of this isotope at the expense of the (αn) reaction in the ea... crust.

The neutron output from the minerals of the earth's crust consists... of neutrons liberated in the spontaneous fission of uranium and neutr... produced in (αn) reactions by the bombardment of the nuclei of light... atoms $(Z < 20)$ by natural alpha particles. Gorshkov and Matvienko... have investigated neutron production in the (αn) reaction on a numbe... of elements by bombarding them with alpha particles emitted by rado... As expected, beryllium gave the highest output. The neutron output from boron and fluorine (CaF_2) is about ten times less and from carb... aluminum and silicon, hundreds of times less than from beryllium. Equally small is the production of neutrons by a piece of granite bom... barded by alpha particles. According to Halpern [2], the cross secti... of the (αn) relation for particles with the energy of about 5 Mev is $4 \cdot 10^{-25}$ cm² for beryllium and $1.5 \cdot 10^{-27}$ for aluminum.

The radioactive elements occur in the earth's crust as oxides or... compounds containing oxygen. In terms of number of atoms, the ear... crust is, on the average, about half oxygen. Therefore, neutron emis... sion as the result of the (αn) reaction on oxygen occurs from all m... erals of the crust on a scale which depends little on their chemical composition. The most important is the reaction of the O^{18} (αn) Ne^2... type. The production of neutrons by the bombardment of oxygen with... alpha particles with the energy of 5 Mev is 0.06 neutrons per 10^6 alp... particle [3], i.e. one thousandth of the neutron output from beryllium. Serdyukova et al. [4] have investigated the (αn) reaction on oxygen. was found that the main contribution is from the O^{18} isotope (30 neutr...

10[6] alpha particles) which constitutes 0.204% of the natural mixture of oxygen isotopes.

Morrison and Pine [5] have investigated the neutron production of uraninite and thorite. The rate of emission is 1.86 ± 0.24 neutrons per minute per gram of uranium and 0.42 ± 0.12 neutrons per minute per gram of thorium. The neutron output per 10[6] alpha particles is 0.30 neutrons for uraninite and 0.27 neutrons for thorite. The author's theoretical computations give 2.5 ± 1 neutrons per 10[6] alpha particles. If a correction is made for neutrons produced by the spontaneous fission of uranium, (which may be neglected for thorium) the output of the (αn) reaction on uraninite is reduced to 0.15 per 10[6] alpha particles. Morrison and Pine's work is the only investigation of neutron production by minerals known to us.

The investigations of the terrestrial neutron flux in underground workings made in 1956-1957 [6, 7] in which the present authors participated, showed the dependence of the flux on the activity and chemical composition of the rocks. The largest flux was recorded in the mines of the Aktyuz deposit (Kirgiziya) where both boron and fluorine are present. Only a weak neutron flux was recorded from inactive rocks. In recent years a number of investigations have been made of the changes in the isotopic composition of rare gases and of the occurrence of the artificially prepared radioactive elements (transuranium elements, radioactive Cl isotopes, technetium etc.) in natural minerals [8]. The main agents of nuclear transformations are neutrons, and for this reason the question of the neutron production by minerals deserves a detailed investigation.

The object of the present work was the determination of neutron emission by various naturally occurring minerals and the clarification of the dependence of neutron output on the content of a radioactive element (uranium or thorium) and on the presence of light elements. The measurements of neutron flux were made by means of a ring of neutron counters submerged in paraffin to slow down the neutrons. The diameter of the cylindrical counter system was 30 cm, its length, ... cm. The counters were divided into two sections each containing counters connected in parallel. The counting rate was recorded separately for each section. This controlled the performance of the apparatus. The SCh-3 instrument was used as the amplifier and counting rate meter. Proportional neutron counters of the SNM-8 type filled with ... were used for measuring. The counters were so placed that they completely surrounded the sample holder. The enrichment of boron with B^{10} was about 87%. The efficiency of the system was determined with the aid of a Po-Be neutron source of known activity placed in the measuring chamber and was found to be 11.8%, thus agreeing with the computed efficiency (12%). The counter system permitted measurement of neutron flux from samples weighing up to 10 kg without noticeable self effect. It could register up to $1 \cdot 10^{-3}$ n/g min.

The background activity consisted of a) cosmic rays neutrons, b) neutrons generated in the paraffin block and in the mass of the sample by

the components of cosmic radiation acting on atomic nuclei, c) false impulses. Inasmuch as our purpose was to measure weak neutron emission, the diminution of the background was an important problem. In order to accomplish this, the apparatus was placed under a 2 meter layer of soil. To decrease the effect of neutrons generated in the soil the system was enveloped in cadmium foil 0.5 mm in thickness, and in an outer 5 cm layer of paraffin. As a result, background activity due to outside neutrons was decreased three times. The maximum value of the background from the neutrons generated in the sample under the action of the cosmic particles was determined by placing 30 kg of lead in the measuring chamber. It turned out that by burying the apparatus under a layer of soil, this effect was diminished ten times, which is in agreement with [9]. The absolute value of the neutron output under these conditions does not exceed $3 \cdot 10^{-4}$ n/g Pb min, which is beyond the sensitivity of the instrument. The average atomic weight of the samples is much less than that of lead, so that the neutrons generated within them can be neglected.

The false impulses may be due to the gamma radiation from the sample and to the alpha particles from the radioactive impurities in the cathodes of the counters. The gamma-ray background rate can be decreased by discriminating between the amplitudes of the pulses so that the pulses from the secondary electrons produced by gamma rays are not registered by the instrument. The determination curves are given in Figure 1 for three cases: 1) Po-Be neutron counter is at a definite distance from the detector, 2) the gamma-ray source, Zn^{65}, with the activity of 2 millicuries is in the measuring chamber and 3) the background rate of the instrument itself.

It develops that with 20v cutoff voltage, the count of the neutron pulses is almost undiminished and the excess of the counting rate with a gamma-ray source over the background amounts to 20 counts/min. Since the activity of the samples was of the order of 10^{-2} millicuries, this component of the background could be neglected. As the result, the background activity of the instrument was due almost entirely to that of the counters and amounted, within the limits of statistical error, to 1. counts/min for each of the counters.

The samples for measuring neutron flux weighed from 100 g to 10 It was important to find out to what extent the neutron output could be slowed down and absorbed by the mass of the sample. To evaluate the possible error from this source, the count rate from the Po-Be neutron source placed in the measuring chamber was compared with the count rate from the same source surrounded by quartz and barite. It was found that for the sizes of the samples used, the change in the neutron flux did not exceed a few per cent. The samples for the measurement of neutron flux were taken from different deposits and can be grouped into 1) inactive samples, containing small amounts of radioactive elements, 2) those containing mainly thorium and 3) uranium-bearing samples. To determine the effect of light elements on neutron production number of mixtures of uranium and thorium minerals with compounds of light elements were prepared.

The content of uranium and thorium in the samples was determined by three methods. The total gamma radiation was measured and by comparison with standards, the amount of radioactive elements in the sample was determined. For this purpose an MS-6 counter surrounded by a lead screen 1 cm in thickness was used. A 100 mg/cm² aluminum filter protected the counter from the effect of beta rays and the soft component of the gamma radiation emitted by the radioactive elements. To determine the absolute amount of the radioactive elements the usual methods of radiochemical analysis of radium isotopes were used.

Fig. 1. Relation between the count rate and cutoff voltage of the discriminator. 1—Po-Be source; 2—γ-source; 3—background.

It was measured by the method of continuous flow of emanations on a compensational setup with electrometers of the Compton type. Radium was determined by the vacuum method on the SG-1M electrometer. Besides this, the content of uranium and thorium, when both were present, was determined by the combined beta-gamma method proposed by Barinov and Shashkina [10]. The same method was used to evaluate the equilibrium of uranium and its daughter products, an evaluation which is necessary in determining the neutron output due to the (αn) reaction. The method is applicable to sufficiently active samples if the thorium-uranium ratio is not too high. The results of the determination of uranium and thorium content by different methods were in satisfactory agreement.

Neutron production depends substantially on the presence of light elements in the sample. At our request, spectrographic analyses of our samples were made by A. I. Lysenko. All minerals from thorium locations contained considerable amounts (of the order of 1%) of fluorine. The content of beryllium was 0.01% on the average.

The results of measurements of the neutron flux from the natural samples are given in Table 1. Altogether 10 uranium and 11 thorium samples were measured. The error of measurement for the samples containing not less than several per cent of radioactive elements amounted to 1-5%, whereas for the weakly radioactive materials it increased to tens of per cent. The table presents the total gamma activity of samples and its ratio to the neutron output. The value of γ/n varies within narrow limits. For thorium minerals the neutron output is somewhat greater per unit gamma activity than for uranium minerals, the average γ/n ratios are 6.7 for thorium and 8.0 for uranium samples (in arbitrary units).
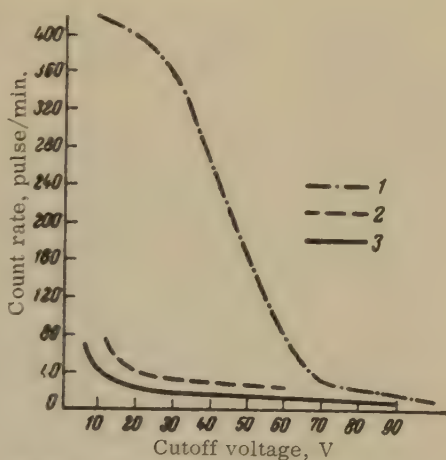
Table 1. Neutron Emission from Natural Samples

No. of sample	Description of sample	γ-emission per 100 g sample pulse/min.	Content, %		Neutron flux per 100 g of sample, n/min.			Neutron flux per 10⁶ α-particles	Ratio γ/n standard units	Content of fluorine %	Relation of neutron flux to fluorine content, in % per 10⁶ α particles
			Th	U	Full flux	Spontaneous emission	(α n) reaction				
	Thorium minerals										
	Ferrithorites										
60-II	Central Kazakhstan	280	29.9	1.4	32.4±1	1.40	31.0	0.6±0.05	8.7	0.34	0.9
62-K	Northern Kazakhstan	332	22.1	2.6	62 ±2	2.5	59.5	1.25±0.1	5.4	0.76	1.1
61-A	Kirgiz, Aktyuz	180	17.4	0.5	26.5±0.8	0.50	26.0	0.9 ±0.06	7.1	1.92	0.3
	Rocks, enriched with ferrithorite										
24-A	Enrichment with Mo and Pb sulfides	1.3	0.1	—	1.1±0.03	—	1.1	7.5 ±0.5	1.2	1.35	5.3
34-A	"	20.5	3.0	0.3	2.7±0.6	0.3	2.4	0.4 ±0.1	7.6	0.87	0.2
36-A	Enrichment with ferrithorite	20.8	1.8	0.03	2.5±0.6	0.04	2.45	0.9 ±0.2	8.3	1.16	0.5
37-A	"	68.6	5.1	0.7	8.7±0.5	0.6	8.1	0.7 ±0.05	7.9	1.3	0.3
38-A	"	10.5	1.7	0.04	1.65±0.4	0.04	1.6	0.6 ±0.2	6.4	0.66	0.45
39-A	Enrichment with black-violet ferrithorite	5.4	0.6	0.02	1.5±0.5	0.02	1.5	1.5 ±0.5	3.6	3.62	0.3
40-A	Enrichment with wax-colored ferrithorite	90.7	14.5	0.6	13.3±0.7	0.7	12.6	0.5 ±0.03	6.8	1.4	0.2
42-A	Enrichment with rare-earth minerals and galens	6.0	0.4	0.02	1.1±0.4	0.02	1.1	1.6 ±0.7	5.5	1.0	1.3
	Uranium minerals										
46	Uranium black	526	0.1	26.8	49 ±8	24.6	24.4	0.15±0.01	10.7		—
140	"	684	—	41.3	84 ±4	38	45.5	0.20±0.01	8.2		—
17-I	Enrichment with pitchblende	86.5	—	4.7	10.4±0.5	4.3	6.1	0.20±0.01	8.3	0.06	—
17-II	"	64.6	—	3.6	11 ±2	3.3	7.5	0.35±0.07	6.0		—
17-IV	"	194.5	0.25	8.4	22 ±3	7.7	14.0	0.3 ±0.04	9.0		—
4	Enrichment with uranium black	84.8	—	4.7	10 ±1	4.3	5.9	0.2 ±0.02	8.4	0.18	—
20	Rocks with high content of radioactive elements	0.8	0.02	0.06	0.2±0.2	0.06	0.14	0.35±0.3	4		—
	Uranium minerals with variable or low content of radium										
70-	Secondary uranium mineral	48.0	0.1	5.1	6.2±0.4	4.7	1.5	0.05±0.01	7.7	0.06	—
80-	Rocks, enriched with secondary uranium minerals	17.0	—	1.5	2.5±1	1.4	1.1	0.12±0.4	6.8		—
30	"	6.5	0.01	0.4	0.6±0.6	0.35	0.25	0.10±0.10	10.8	0.001	—

The table gives the total neutron flux, the flux produced by the (αn) reactions and the flux computed for 10^6 alpha particles. It also shows the fluorine content and the ratio of the flux to the alpha radiation computed per unit of fluorine.

The neutron production by the radioactive minerals reaches 0.84 min per gram of rock. The neutron output per 10^6 alpha particles is -1.6 (0.9 ± 0.2 on the average) for thorium minerals, and from 0.30 to 0.50 (0.39 ± 0.03 on the average) for uranium minerals. An exception is sample 24-A with a very high neutron output (7.5 per 10^6 particles). The thorium oxide in equilibrium with its decay products, according to our calculations, emits 0.2 ± 0.05 n per 10^6 alpha particles so the relatively high neutron output from thorium minerals is evidently related to the presence of fluorine. However, in general, neutron output per 10^6 alpha particles is not proportional to the fluorine content. The neutron emission depends strongly on the distribution of thorium and fluorine in a given sample as can be judged from the change in neutron output from comminuted samples. Even the samples of ferrithorite homogeneous to the eye increase their neutron output about 1.5 times on being powdered (sample 60-Ts, from 0.6 to 0.9, sample 61-A from 0.9 to 1.23 neutrons per 10^6 alpha particles). For samples of rock containing ferrithorite, this increase is even greater, from 13.3 to 23.4 neutrons per 100 g of rock (sample 40-A).

Thus, the neutron emission of the investigated thorium minerals is determined mainly by the $F^{19}(\alpha n)Na^{22}$ reaction. The number of neutrons from the $O^{18}(\alpha n)Ne^{21}$ reaction is, on the average, about 30% of the total. The neutrons produced by other reactions and by spontaneous fission may be neglected.

In the investigated samples, uranium (except for the non-equilibrium secondary minerals) occurs in the form of oxides, and the neutron emission is due apparently to the reaction on O^{18}. The variation in the neutron output for most of the samples of average size almost equals the error of observation. The neutrons from the $O^{18}(\alpha n)Ne^{21}$ reaction are emitted at the rate of 0.15 to 0.35 (0.23 ± 0.03 on the average) per 10^6 alpha particles. Thus, within the limit of error, the neutron output from this reaction is the same for alpha-radiation for both the thorium and uranium series. The neutrons produced by spontaneous fission of uranium are emitted at the rate of 0.92 neutrons per minute per one ton of uranium or 0.15 neutrons per 10^6 alpha particles of uranium in equilibrium with its daughter elements, which constitutes 30 to 50% (40% on the average) of total neutron flux from the uranium sample.

In order to evaluate the effectiveness of the (αn) reaction on individual light elements, we investigated neutron emission from certain uranium (17-Iv) and thorium (60-Ts, 61-A) minerals mixed with light element compounds, namely, with beryl ($Be_3Al_2Si_6O_{18}$), fluorite (CaF_2), aluminum and magnesium oxides, quartz (SiO_2) and barite ($BaSO_4$). These minerals were added in amounts from 50 to 1500% of the mass of the sample in order to obtain 10-, 20-, 30- etc. per cent content of the light elements (Be, Al, Mg, Si and Ba) in the mass of the mixture. The
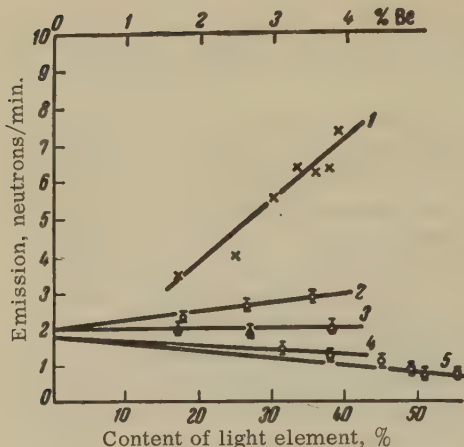
Fig. 2. Neutron emission from ferrithorite mixture containing compounds of light elements. 1—Be; 2—Al; 3—Mg; 4—Si; 5—Ba
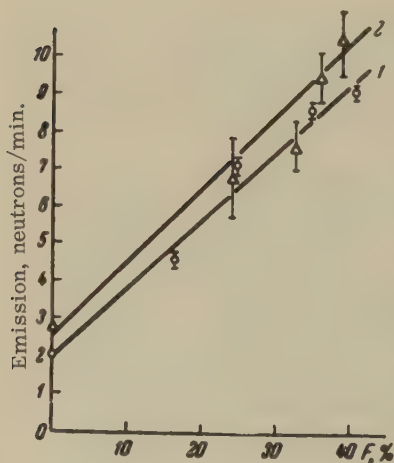
Fig. 3. Neutron emission from fer-rithorite (curve 1) and pitch-blende (curve 2) mixtures with fluorite.

results of measurements of neutron flux from these mixtures are given in Figure 2.

The neutron output from a mixture depends strongly on the degree of comminution of the sample. This is very clearly shown by the mixture of pitchblende and fluorite. For the coarse-grained mixture (particle size of the order of 100 μ), the neutron output was 14 n/min but for the same mixture reduced to fine powder, it increased to 41 n/min, i.e., almost threefold. The measurements of all mixtures described in the table were made after grinding them in a ball mill to the particle size of the order of a few microns, which is several times less than the travel distance of the alpha particles in the mineral.

In a mixture containing 2.5% beryllium, the neutron output from the Be^9(αn) C^{12} reaction per one gram of uranium is 2.5 n/min and per gram of thorium, 1.7 n/min. On increasing the beryllium content, the neutron output from thorium minerals increased linearly. The computed neutron output per 10^6 alpha particles is 17 neutrons for the uranium series and 46 for the thorium series, i.e. the probability of (αn) reaction on beryllium for natural minerals is approximately one hundred times as great as on oxygen.

The neutron emission from a mixture of beryllium with radioactive minerals is basically determined by the (αn) reaction. We investigated the neutron output due to the (γn) reaction by surrounding the mineral with the same amount of beryllium as was taken for making the mixture. The relative number of neutrons from the (γn) reaction constitutes 11% of the neutrons from the (αn)

sample	Radioactive mineral	Amt. radio-active mineral g.	Added mineral	Amt. added material, g.	Content of Th or U, g.	Amount mineral studied in mixture, %	neutron emission, n/min.	neutron emission per 1 g.U or Th per minute
60-II	Ferritorite	160	Beryl	80	39 Th	1.7 Be	132±6	3.4±0.15
60-II	"	160	"	160	39 Th	2.5 Be	157±7	4.0±0.2
60-II	"	160	"	240	39 Th	3.0 Be	214±7	5.5±0.2
60-II	"	160	"	320	39 Th	3.3 Be	248±7	6.4±0.2
60-II	"	160	"	400	39 Th	3.6 Be	241±7	6.2±0.2
60-II	"	160	"	480	39 Th	3.8 Be	243±7	6.3±0.2
60-II	"	160	"	560	39 Th	3.9 Be	283±7	7.3±0.2
60-II	"	160	Fluorite	80	39 Th	16.2 F	180±6	4.6±0.15
60-II	"	160	"	160	39 Th	24.3 F	278±7	7.1±0.2
60-II	"	160	"	420	39 Th	34.5 F	335±6	8.6±0.15
60-II	"	160	"	850	39 Th	40.5 F	354±7	9.1±0.2
60-II	"	160	Al_2O_3	80	39 Th	17.7 Al	91±6	2.3±0.15
60-II	"	160	"	160	39 Th	26.5 Al	106±5	29.7±0.1
60-II	"	160	"	320	39 Th	35.5 Al	114±5	2.9±0.1
60-II	"	160	MgO	67	39 Th	17.5 Mg	82±6	2.1±0.15
60-II	"	160	"	135	39 Th	27 Mg	80±5	2.0±0.1
60-II	"	160	"	300	39 Th	39 Mg	83±5	2.1±0.1
17-IV	Pitchblende	70	Beryl	70	6.0 U	2.5 Be	36±5	6.0±0.8
17-IV	"	70	Fluorite	70	6.0 U	24.2 F	41±6	6.8±1.0
17-IV	"	70	"	140	6.0 U	32.4 F	46±4	7.7±0.7
17-IV	"	70	"	210	6.0 U	35.7 F	57±4	9.5±0.7
17-IV	"	70	"	280	6.0 U	38.6 F	63±6	10.5±1.0
61-A	Ferritorite	200	SiO_2	450	37 Th	32.5 Si	54±5	1.5±0.1
61-A	"	200	"	900	37 Th	38 Si	49±5	1.3±0.1
61-A	"	200	$BaSO_4$	300	37 Th	36 Ba	52±5	1.4±0.1
61-A	"	200	"	600	37 Th	45 Ba	40±5	1.4±0.1
61-A	"	200	"	900	37 Th	49 Ba	35±5	0.9±0.1
61-A	"	200	"	1200	37 Th	51 Ba	28±5	0.8±0.1
61-A	"	200	"	1500	37 Th	53 Ba	34±5	0.9±0.1
61-A	"	200	"	3000	37 Th	56 Ba	29±5	0.8±0.1
60-II	Pitchblende	160	—	—	39 Th	—	76±4	2.0±0.1
17-IV	Pitchblende	70	—	—	6 U	—	16±2	2.7±0.3
61-A	Ferritorite	200	—	—	37 Th	—	71±2	1.9±0.05

reaction for thorium minerals and 19% for uranium minerals. It is well known that for natural gamma radiation, reactions of the (γn) type are possible on deuterium and Be^9 only.

A much smaller neutron output due to alpha radiation was found in aluminum and magnesium. Calculations show that 1% aluminum content increases neutron output, on the average, by 0.025 neutrons per min per gram of Th. Addition of magnesium oxide practically does not increase the output, and addition of silicon in the form of quartz and especially of barium sulfate (barite) substantially decreases neutron emission (Figs. 2, 3). The data are insufficient to evaluate the probability of a (αn) reaction on different elements, but it may be remarked that the probability of reaction is greater for aluminum than for the average material of the rock, whereas for silicon and barium it is less.

The decrease in neutron output on addition of quartz and barite indicates also that the probability of (αn) reaction on oxygen is less than the probability of reaction on the rock as a whole. This confirms our conclusion that fission of fluorine plays an important role in the neutron emission from ferrithorites. For magnesium, evidently, the probability of reaction is a little higher than for oxygen because, with the dilution of ferrithorite with magnesium oxide, the neutron emission remains practically unchanged. Evidently, dilution with a large amount of a substance decreases neutron emission of the mixture and causes neutron absorption.

As can be seen from Table 2, in the first approximation the neutron output changes linearly, with increase in the content of the target-mineral. In the case of considerable amount of admixtures, the neutron flux tends towards saturation, i.e. towards a complete replacement of the substance of the mineral by the admixed material.

Fluorine is of especial interest as a target-element for it is a constituent of the investigated thorium minerals. In making mixtures of a radioactive element with fluorine, it was found that the additional production of neutrons from the (αn) reaction on fluorine was the same for uranium and thorium and amounted to 0.2 n/g of the radioactive element per minute with 1% of fluorine in the mixture. The neutron output referred to the alpha particles is approximately 3 to 4 times as great for the thorium as for the uranium minerals. This may possibly be due to the greater energy of the alpha particles of the thorium series. On addition of fluorine, the neutron output is about ten times less than on addition of an equal amount of beryllium, and this agrees with the data of [1, 3].

The data on neutron emission from mixtures of radioactive minerals and compounds of light elements show that the effectiveness of the (αn) reaction on different elements may be represented by the following series: Be > F > Al > Mg > the average material of ferrithorite > O > The main components of natural minerals are oxygen, silicon and aluminum. Fluorine and beryllium are, respectively, 600 and 50,000 times less abundant than oxygen, and the neutron production from the fission of these elements can occur only in minerals enriched in them.

Wetherill [11] discovered that old radioactive minerals have higher ratios of Ne^{21} and Ne^{22} to Ne^{20}. Enrichment in Ne^{21} has been demonstrated for three different minerals (uraninite, monazite and euxenite) and enrichment in Ne^{22} for only one (euxenite). The author believes that the excess of neon was formed as the result of (αn) reactions on O and F^{19}. It is probable that euxenite contains a considerable amount of fluorine.

Knowing the activity and age of minerals and using our data on neutron production, i.e. the data on the rate of formation of neon isotopes, it can be shown that the neon content in minerals must be tens of times higher than found by Wetherill. The loss of helium from the minerals studied by him amounts to 70 to 90% as shown by the ratio of the helium and lead ages. However, neon should be emitted by minerals in much smaller amounts than helium, and Wetherill's data on the neon content may be too low because of incomplete liberation of the gas.

The formation of Ne^{21} from the (αn) reaction is, evidently, the principal process of accumulation of the products of transmutation of atomic nuclei in the earth's crust. Assuming that the average content of uranium in the lithosphere is $1.3 \cdot 10^{-6}$ g/g and of thorium $5.0 \cdot 10^{-6}$ g/g [7], we see that, on the average, in 1 g of substance 2.1 atoms of Ne^{21} are formed per year. The error in the determination of this value is about 20%. Using the average content of potassium (1.6%), it can be calculated that the formation of argon per one gram of matter averages about $1.7 \cdot 10^6$ atoms of A^{40} per year. The ratio of the two gases is $A^{40}/Ne^{21} = 8 \cdot 10^5$. It is known that the presence of argon in the earth's atmosphere is due entirely to the liberation of radiogenic argon. Neon, as a lighter element, must be liberated by minerals in greater amounts on the average than argon. If it is considered that the atmosphere contains $9.8 \cdot 10^{41}$ atoms of radiogenic argon and $5.1 \cdot 10^{36}$ atoms of Ne^{21} [12], then it follows from the ratio given above that not less than $1.23 \cdot 10^{36}$ Ne^{21} atoms or not less than 25% of Ne^{21} in the earth's atmosphere is of radiogenic origin.

The neutron output measured by us (of the order of 0.2 neutrons per million alpha particles) is near to that measured by Morrison and Pine[5], according to our data, the neutron emission is due mainly to the O^{18} $(\alpha n) Ne^{21}$ reaction. The theoretical output of this reaction given by Morrison and Pine is too low. Using it, Damon and Kulp [12] arrived at the incorrect conclusion that the content of radiogenic Ne^{21} in the earth's crust is very low (less than 1%).

Ne^{21} and He^3 are the only isotopes in the earth's crust whose presences are due essentially to the processes of nuclear transmutations.

The results of measurements of the neutron flux from inactive minerals are given in Table 3. The average neutron output is less than the limits of measurement of the apparatus. Barite (Kvais) and galena (Mirgalimsai Kok-su) give a somewhat high value for the flux, perhaps because of the more intensive generation of neutrons under the action of the hard components of cosmic rays. The samples from Akchatau are noteworthy. As was pointed out in a previous paper [6], the neutron flux in

Table 3. Neutron Emission from Weakly Radioactive Samples

Description and locality of sample	Weight of sample, kg	Neutron emission n/min.	Neutron flux per 100g sample n/min.
Molybdenite with quartz, Dastakert	10.5	1.0± 3.5	< 0.1
Bornite, Dastakert	7.5	2 ± 3.5	~ 0
Ore-vein minerals, Dastakert	6.0	1.0± 3.5	< 0.1
Chalcopyrite, Kafan	11.0	6 ± 4	~ 0
Chalcopyrite concentrate, Kadzharan	9.0	2 ± 4	~ 0
Barite, Kveisa	12.0	5 ± 4	0.05± 0.04
Molyboenite, Kadzharan	7.0	2 ± 4	~ 0
Rock from radioactive source (1000γ), Kadzharan	4.0	5 ± 5	~ 0
Pyrite, Akchatau	8.0	5 ± 2.5	0.06± 0.03
Pyrite and fluorite, Akchatau	12.5	7 ± 4	0.06± 0.03
Quartz with molybdenite, Central Talgar	9.0	3.5± 3.5	~ 0
Galena, Kok-Su	3.5	2.5± 3.5	0.07± 0.1
Molybdenite, Eastern Kounrad	7.5	1 ± 4	~ 0
Rock from albite vein, Eastern Kounrad	5.0	1 ± 6	0.015± 0.1

underground workings was up to one tenth of the neutron flux on the surface. The minerals from this locality also give higher values of neutron output as compared with other weakly active samples. It is probable that this is due to a higher content of fluorine.

SUMMARY

The neutron emission by radioactive minerals has been investigated. For ferrithorites the average neutron output is 0.9 ± 0.2 neutrons per 10^6 alpha particles and for uraninites it is 0.39 ± 0.03 neutrons per 10 alpha particles. It is shown that about 40% of the neutrons in the emission from the uranium minerals is generated by spontaneous fission.

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RADIOACTIVE ELEMENTS IN OIL FIELD WATERS

F. A. Alekseev, V. I. Ermakov, and V. A. Filonov

Petroleum Institute,
Academy of Sciences USSR, Moscow

Abstract

New data on the content and distribution of uranium and radium in the water
of oil fields of the platform and the folded area, as well as of beds related to re
and salt dome structures, have been considered. For all types of fields simila
radium concentrations (n x 10^{-10} g/l) and a low uranium content, rarely excee
ing 1.0 x 10^{-7} g/l, have been noted; this ratio is considerably higher than the
equilibrium ratio in the radium concentration in bed waters with increasing dis
tance from the oil field as well as in the case of a prolonged exploitation of the
field has been noted. A decrease of the radium content in the upper water-bea
horizons with a relative uranium increase has been observed. These pecularit
in the radium and uranium contents in waters of oil fields are due to the specifi
geochemical conditions typical to oil fields.

An investigation of the radioactivity of oil well waters in some of th
petroliferous regions of the Soviet Union, conducted in the 30's by the
State Radium Institute and other organizations, established the existen
of a very important form of concentration of uranium on the earth's s
face which in V. I. Vernadskii's opinion [1] exceeds the largest deposi
of radium ores. It has been stated [2] that oil field waters have the
highest radium concentration, 10^{-8} to 10^{-10} g/l, of all ground waters.
Besides radium these waters contain ThX and MsThI. Recent investi
gations [3, 4] show that the radium of oil field water is leached out of
rocks with a normal content of dispersed radioactive elements, that
waters of the sodium-calcium chloride type aid in the desorption of r
dium and that the usual low uranium content in these waters is due to
its presence in the rocks in its very insoluble tetravalent form.

In spite of the extensive investigations of the radioactivity of wate
the existing literature on the subject does not provide definite inform
tion on the distribution of the radioactive elements in the oil fields in
relation to the differences in geologic structures and to the chemistr
of the oil field waters.

The recent development of radiometric methods of prospecting fo
petroleum and gas in the Soviet Union and abroad makes investigation
of the radioactivity of rocks and waters of the oil fields an important
phase of exploration. In the opinion of some investigators [5], the ra
dioactive anomalies observed on the surface of the earth are caused
vertical migration of uranium and radium contained in ground waters

vicinity of petroleum deposits. On the other hand, the redistribution
radioactive elements over oil pools may be due to the effect of the
chemical environment created by petroleum and gas [6].

The Laboratory of Nuclear Geophysics and Geology of the Petroleum
Institute has for a number of years conducted a study on the radioactiv-
of waters in the different petroliferous provinces of the Union. The
material presented below on the content of Ra and U in the waters of
investigated petroliferous provinces leads to certain conclusions
concerning the radioactivity of waters in oil fields with different geo-
ic structures and concerning the areal distribution of radioactive
ments in these waters.

The determinations of Ra in the waters were made by the usual ra-
chemical method [3], by measuring radon with the SG - IM electrom-
r. The sensitivity of the method was of the order of 10^{-13} g/l with
precision of measurement of ±10%. Uranium was determined by
luminescence. It was precipitated from the samples with aluminum po-
assium sulfate and measured by fluorescence in ultraviolet light. The
sitivity of this method under laboratory conditions was up to $1 \cdot 10^{-8}$

WESTERN TURKMENIYA

In Western Turkmeniya water from the oil wells of the Kum-Dag oil
field was investigated. Analyses were made of waters from 23 wells
penetrating the petroliferous horizons of the Apsheron and Akchagyl
ges and of the Pliocene redbeds. In addition, waters from explora-
ory drillholes and from the springs of the Boyadag structure in the
imir-Okarem area were studied, as well as waters from water wells
and mud volcanoes.

The ground waters of the petroliferous areas of Western Turkmeniya
long mainly to the calcium chloride type* with a high content of dis-
ved salts amounting to 200-10,000 mg-equiv. The dissolved salts are
ium, calcium and magnesium chlorides. All waters are character-
by a high $\dfrac{Cl - Na}{Mg}$ ratio which reaches 22.78 and are either sulfate-
or contain very small amounts of sulfates, up to 20 mg-equiv.

The investigated basal and high horizon waters of the Kum-Dag oil
field are characterized by a high radium content ranging from $1.03 \cdot$
10^{-10} to $6.15 \cdot 10^{-10}$ g/l (Table 1). There is no noticeable variation in
um content either areally or with depth and most analyses give $1.2 \cdot$
10^{-10} g/l Ra. The highest concentration ($6.15 \cdot 10^{-10}$ g/l) was found in
#194, which reaches horizon V of the redbed sequence. The ura-
m content of these waters is low, not over $2.0 \cdot 10^{-7}$ g/l. The Ra/U
io is of the order of 10^{-2} to 10^{-3}, i.e. considerably higher than the
librium ratio ($3.36 \cdot 10^{-7}$).

ording to A. V. Sulin's classification.

Table 1

Location of sample	Chemical composition, mg-equiv.							$\frac{Cl-Na}{Mg}$	Ra, g/l	U, g/l
	Cl	SO$_4$	HCO$_3$	Ca	Mg	Na+K	Σr			
Kum-Dag. Apsheron formation, well 361	1610	—	1	180	31	1400	3222	6.78	$1.3 \cdot 10^{-10}$	—
Kum-Dag. Apsheron formation, well 500	2580	1	2	305	135	2143	5166	3.23	$1.03 \cdot 10^{-10}$	—
Kum-Dag. Apsheron formation, well 341, hor. V	2480	—	2	273	154	2057	4968	2.7	$1.25 \cdot 10^{-10}$	$1.75 \cdot 10^{-7}$
Kum-Dag. Apsheron formation, well 237, hor. V	2750	—	1	292	187	2272	5502	2.5	$1.7 \cdot 10^{-10}$	$2.0 \cdot 10^{-7}$
Kum-Dag. Apsheron formation, well 361, hor. G	3080	—	1	327	211	2543	6162	2.5	$1.67 \cdot 10^{-10}$	$3.5 \cdot 10^{-6}$
Kum-Dag. Akchagyl formation, well 294	2200	—	1	254	114	1833	4402	3.22	$1.20 \cdot 10^{-10}$	—
Kum-Dag. Akchagyl formation, well 522, hor. V	2700	—	—	397	99	2244	5480	5.00	$1.15 \cdot 10^{-10}$	—
Kum-Dag. Krasotsvetnaya series, well 194, hor. V	1680	—	1	176	50	1455	3362	4.5	$6.15 \cdot 10^{-10}$	$1.75 \cdot 10^{-}$
West. Kum-Dag. Krasnotsvetnaya series, well 575	2904	—	2	276	232	242.5	3666.5	2.0	$2.45 \cdot 10^{-10}$	$2.0 \cdot 10^{-}$
Kum-Dag. Krasnotsvetnaya series, well 56, hor. V	2510	—	2	361	76	2075	5024	5.69	$2.80 \cdot 10^{-10}$	$1 \cdot 10^{-}$
Boya-Dag. Well No. 1	4420	1	1	996	187	3240	8844	6.94	$2.25 \cdot 10^{-10}$	—
Boya-Dag. Well No. 2	3620	1	1	655	110	2857	7244	6.94	$1.14 \cdot 10^{-10}$	—
Boya-Dag. Well No. 8	3600	2	1	659	115	2829	7201	6.69	$8.38 \cdot 10^{-11}$	—
Keimir-Chikishlyar region, Well No. 9	2920	14	1	650	276	2009	5870	3.30	$7.66 \cdot 10^{-10}$	—

A similar concentration of radium was found in the waters of the Boya-Dag springs with high mineral content and in the borehole water. In the Keimir-Chikishlyar petroliferous region the maximum ($7.66 \cdot 10^{-10}$) radium content was measured near the village of Keimir, in an exploratory hole spouting hot brine with films of oil.

It should be noted that the radium content of the investigated ground waters bears no evident relation to their mineral content. For example, in the Kum-Dag region the radium content is the same everywhere, whereas the mineral content varies from 3000-6000 mg-equiv.

A very high radium content characterizes oil well waters of the Cheleken field investigated in the early 30's by Tageeva, Starik and Cherdatov [7, 8]. Here the radium content ranges from 2.6 to $6.75 \cdot 10^{-10}$ with this range remaining constant throughout the section of the oil well.

Thus all investigated ground waters in the productive horizons of the oilfields of Western Turkmeniya have high radium content of the order of $\cdot 10^{-10}$ g/l. It is noteworthy that similar radium concentrations are found in other petroliferous regions of the geosynclinal type composed of Tertiary sediments. Thus, the waters of the productive horizons of the Shor-Su region (Fergana basin) contain 1.7 to $4.3 \cdot 10^{-10}$ g/l [9]. For the Novo-Groznensk region [10, 11] the figures, $8.38 \cdot 10^{-11}$ and $7.6 \cdot 10^{-10}$ g/l have been cited.

In the surface waters of Western Turkmeniya the radium content is from 100 to 1000 times lower than in the ground waters and ranges from $1.0 \cdot 10^{-13}$ g/l to $2.42 \cdot 10^{-12}$ g/l, whereas the uranium content increases to $5.75 \cdot 10^{-6}$ g/l. The data on the composition and the content of radioactive elements in the surface waters are given in Table 2. The U ratio in these waters is lower than in ground waters and amounts to 10^{-5} to 10^{-6} but still does not reach the equilibrium ratio.

Table 2

No.	Location of sample	Chemical composition, mg-equiv.							Na Cl	Ra, g/l	U, g/l
		Cl	SO₃	HCO₃	Ca	Mg	Na+K	Σr			
	os. Keimir (hole)	4120	19	1	862	911	2377	8280	0.57	$1.0 \cdot 10^{-12}$	
	os. Keimir (hole)	2850	4	1	346	843	1666	5710	0.58	$2.42 \cdot 10^{-12}$	$1 \cdot 10^{-7}$
	os. Keimir (hole)	2030	15	2	238	537	1272	4094	0.62	$2.42 \cdot 10^{-12}$	$1 \cdot 10^{-7}$
	k-Patlaukh (hole)	2910	34	4	98	609	2241	5896	0.77	$2.6 \cdot 10^{-12}$	$5.75 \cdot 10^{-6}$
	k-Patlaukh (hole)	2170	5	3	42	478	1658	4356	0.76	$1.42 \cdot 10^{-12}$	—
	hodzha-Makhum, shaft	125	22	3	32	37	81	300	0.65	$1.0 \cdot 10^{-12}$	$5.25 \cdot 10^{-7}$
	derlen, shaft	4.2	4.0	5.0	5.0	1.0	7.2	26.4	1.71	$1.04 \cdot 10^{-12}$	—
	ara-Tepe, shaft	4.8	31.0	2.2	22.8	1.2	14.0	76	1.87	$2.27 \cdot 10^{-12}$	—
	derlen, shaft	7.7	1.3	5.0	3.0	1.0	10.0	28	1.28	$1.0 \cdot 10^{-12}$	—
	oshadzha-Kui, shaft	2.7	3	4.6	4.4	1.2	4.7	20.6	1.74	$6.04 \cdot 10^{-13}$	$1.25 \cdot 10^{-6}$
	oradzha-Batyr, shaft	0.8	2	4.6	3.6	1.0	2.8	14.8	3.50	$1.71 \cdot 10^{-12}$	—
	hali-Kuruk, shaft	5.8	14.0	3.2	7.8	2.6	12.6	46.0	2.17	$1.47 \cdot 10^{-12}$	$1.25 \cdot 10^{-7}$
	k-Patlaukh, shaft	96	23	3	33	5	84	244	2.55	$1.48 \cdot 10^{-12}$	1.10^{-7}

The maximum mineral content in the surface waters (4094-8280 mg-equiv.) is found in the salt pans where water is drawn from shallow wells and the minimum mineral content, in numerous water wells, (- 244.0 mg-equiv.). The concentration of radioactive elements in waters has no relation to their mineral content.

A special position is held by waters of mud volcanoes (Table 3). These waters are sodium carbonate and calcium chloride types and have high mineral content ranging from 938 to 4020 mg-equiv.

Table 3

No. of sample	Location of sample	Chemical composition, mg-equiv.							$\frac{Na}{Cl}$	$\frac{Na-Cl}{SO_4}$	Ra, g/l	U, g/l
		Cl	SO$_4$	HCO$_3$	Ca	Mg	Na+K	Σr				
2	Well on the slope of AK-Patlaukh mud volcano	1478	27	20	3	14	1508	3050	1.02	1.11	$1.0 \cdot 10^{-12}$	$1.25 \cdot 10^{-}$
31	Inside crater of Kipyashchii bugor mud volcano	403	14	71	6	21	461	976	1.14	4.13	$2.1 \cdot 10^{-12}$	$8.7 \cdot 10^{-}$
24	Inside crater of Kainakh mud volcano	440	13	16	7	5	457	938	1.05		$9.0 \cdot 10^{-12}$	$1 \cdot 10^{-}$
25	Inside crater of Ak-Patlaukh mud volcano	1990	16	4	86	29	1895	4020	0.95		$1.0 \cdot 10^{-12}$	$1 \cdot 10^{-}$

Typically, the sodium carbonate waters have a high uranium content, which apparently occurs in them in the form of easily soluble bicarbo ates. The sodium chloride waters are relatively enriched in radium, which is characteristic of the ground waters of this type.

THE EMBA PETROLIFEROUS PROVINCE

The waters of the salt dome oil fields analyzed for their content of radioactive elements came from the productive Lower Cretaceous, J rassic and Permo-Triassic horizons. They are of the calcium chlori type. Their mineral content usually increases with depth and is espe cially high near the salt plugs. The absence of sulfates and the pre- dominance of chlorine over sodium (the Na/Cl ratio is less than one) are characteristic. Table 4 presents a number of typical analyses of

Table 4

No. of sample	Formation	Chemical composition, mg-equiv.							$\frac{Na}{Cl}$	N S
		Cl	SO$_4$	HCO$_3$	Ca	Mg	Na+K	Σr		
22	Teren-Uzyuk, Well, 17	1359.0	0.77	0.18	171.06	27.29	1161.60	2719.90	0.85	7
23	Munaili, Well 36	993.28	18.67	5.12	2.53	1.58	1013.25	2034.73	0.88	7
24	Munaili, Well 52	3559.90	5.3	0.76	175.08	101.25	3289.63	7131.91	0.93	

these waters. The waters of the Karaton, Teren-Uzyuk, Kulsary and Munaili oil fields were analyzed for their content of radioactive ele- ments. All sampled waters have a high radium content ranging from $1.37 \cdot 10^{-11}$ to $7.92 \cdot 10^{-10}$ g/l. Their uranium content is less than 10^{-8} g/l. Comparison of radium content according to stratigraphic sampling intervals (Table 5) shows no significant variation.

The lowest radium content in the Emba region was measured in t Munaili field, where it decreases from $8.78 \cdot 10^{-11}$ g/l to $3.4 \cdot 10^{-12}$

also, the char-
istic decrease in
m concentration
from the oil pool
observed. Thus,
aters in the Al-
Cenomanian beds
level of the pool
in $1.37 \cdot 10^{-11}$
a, whereas at
distance from
ool the radium
nt is $3.09 \cdot 10^{-13}$

Table 5

No. of sample	Formation	Horizon	Content of Ra, g/l
29	Karaton	Alb.	$2.0 \cdot 10^{-10}$
30	"	"	$7.92 \cdot 10^{-10}$
36	"	"	$1.36 \cdot 10^{-10}$
33	"	Apt.	$5.34 \cdot 10^{-10}$
38	"	Neokom.	$3.72 \cdot 10^{-10}$
31	Kulsary	Jura.	$3.18 \cdot 10^{-10}$
37	"	Permo-Trias.	$7.73 \cdot 10^{-10}$

OIL FIELDS OF PRE-URALIAN DOWNWARP

this region the waters of the Artinskian petroliferous reefs and of
imian redbeds were investigated. The investigated ground waters
ines of the calcium chloride type. Their mineral content ranges
7791 to 10686 mg-equiv. Notable are the high content of chlorides,
o 5301 mg-equiv, and the rather low content of sulfates, 38 mg-
The results of analyses of these waters for radioactive elements
ven in Table 6.

Table 6

No. of sample	Formation	Content of Ra, g/l	Content of U, g/l
5	Ishimbaevo, well 95	$4.8 \cdot 10^{-11}$	$7.5 \cdot 10^{-7}$
6	Ishimbaevo, well 97	$3.19 \cdot 10^{-11}$	$< 1 \cdot 10^{-8}$
26	Ishimbaevo, well 103	$3.18 \cdot 10^{-11}$	$< 1 \cdot 10^{-8}$
9	Vvedenovskoe, well 145	$9.61 \cdot 10^{-11}$	$< 1 \cdot 10^{-8}$
8	Tereklov, well 505	$5.35 \cdot 10^{-10}$	$< 1 \cdot 10^{-8}$
7	Kazankov, well 97	$2.24 \cdot 10^{-10}$	$< 1 \cdot 10^{-8}$
27	Kinzebulatov, well 114	$1.63 \cdot 10^{-10}$	$< 1 \cdot 10^{-8}$

analyses show high radium content in these waters which varies
.18 · 10^{-11} to $5.35 \cdot 10^{-10}$ g/l. The concentration or uranium does
ally exceed $1.0 \cdot 10^{-8}$ g/l but in one case rises to $7.5 \cdot 10^{-7}$ g/l.
lowest radium content was found in the oil well waters of the
ai oil field. This may be explained by the hydrogeological isola-
these waters, for to the south of the Ishimbai reef complex the
the top of the Artinskian sediments and the thickness of the
ng strata increase considerably. Simultaneously with the in-

in radium content, the $\frac{Cl-Na}{Mg}$ ratio (coefficient of metamorphism)

Table 7

No. of sample	Location of sample	Chemical composition, mg-equiv.							$\frac{Na}{Cl}$	$\frac{Na-Cl}{SO_4}$	Ra, g/l	U, g/l
		Cl	SO$_4$	HCO$_3$	Ca	Mg	Na+K	Σr				
1	Well No. 1	0.20	14.06	7.80	1.00	1.50	19.50	11.12	100.7	1.38	$5.15 \cdot 10^{-13}$	$4.5 \cdot 10^{-6}$
3	Well No. 2	1.39	8.92	0.70	1.00	1.72	14.53	34.50	10.43	1.47	$3.29 \cdot 10^{-12}$	$1.05 \cdot 10^{-5}$
4	Well No. 5	1.17	7.89	5.88	1.20	2.44	11.31	29.89	9.63	1.28	$9.27 \cdot 10^{-13}$	$4.5 \cdot 10^{-6}$

also increases. This decrease in radium concentration, however, may be due to the longer exploitation of the Ishimbai oil field, which has been active since the 1930's. Decrease in radium concentration with exploitation of an oil field is not uncommon.

Nikitin [9] pointed out that the waters of the productive horizons of the Sel-Rokho field, which has been worked for 20 years, are impoverished in radium as compared with the waters of the Sho Su field exploited for only three years. Komlev [11] also cites data on the decrease of radium with water withdrawal from the basal water-bearing horizon. This phenomenon is due, undoubtedly, to the enrichment of waters in radium at the level of the oil pool. As these waters are withdrawn, waters from other levels move in and the radium concentration decreases.

The basal water-bearing horizons of the Artinskian horizon were studied also in the Kinzeł oil field located in the belt of brachyanticlines* in the eastern part of the Pre-Urals downwarp. The radium content here, as in all waters of the petroleum-bearing reef complex, is high and amounts to $1.63 \cdot 10^{-10}$ g/l.

The surface waters in the Vvedenovsk area were studied in the springs located in the Ufimian red beds. These waters are of the sodium carbonate type and have relatively low mineral content (up to 44.0 mg-equiv.), low chlorinity and a considerable content of hydrous sodium carbonate. The Na/Cl ratio has high values (from 10 to 100). All of the waters have a low radium content, ranging from $1.03 \cdot 10^{-13}$ to $3.29 \cdot 10^{-12}$ g/l. There is a reciprocal relationship between radium content and the Na/Cl ratio, which indicates the degree of freshening of the water. The uranium content increases correspondingly to $1.06 \cdot 10^{-5}$ g/l (Table 7).

THE PLATFORM PETROLIFEROUS REGIONS

As a characteristic example, the data on the waters of the Shkapo oil field in the Bashkir ASSR may be presented. The analyzed water came from beds I and IV of the Devonian Pashiisk formation and from

*A U.S.S.R. term meaning "a long, narrow anticline."

springs in the Upper Permian Kazanian sediments. The ground wa-
ters are of the calcium chloride type, have high mineral content of 3503-
3 mg-equiv, high content of chlorides and low content of sulfates.
The radium content in bed D_1 (borehole 29) is up to $2.82 \cdot 10^{-10}$ g/l
in bed D_{IV} (borehole 92), $4.73 \cdot 10^{-10}$ g/l. Both boreholes are at the
level. It is notable that with the increase in radium content in bed
the $\frac{Cl-Na}{Mg}$ ratio increases from 1.26 to 6.26. The radium content
creases sharply with the distance from the oil pool. Thus, in bore-
17, located 2.5 km from the contour of the oil pool, the radium con-
in the water of bed D_1 decreases to $8.34 \cdot 10^{-12}$ g/l while the gen-
chemical composition of water remains the same.

The Devonian ground waters were studied also in the Serafimovsk oil
of the Bashkir ASSR. Here, also, the radium content is high and
ches $2.59 \cdot 10^{-10}$ g/l (bed D_1). The uranium content is low in all
ples and lies within the limit of analytical error, $10 \cdot 10^{-8}$ g/l.

The waters of the Kazanian sediments were studied both within and
ide of the petroliferous area. All waters are of the sodium carbon-
type, are low in mineral content which ranges from 9 to 21 mg-
v., have low chlorinity and low sulfate content. The $\frac{Na}{Cl}$ ratio varies
5 to 45. The radium content in the investigated waters varies
1.03 $\cdot 10^{-13}$ to $3.50 \cdot 10^{-12}$ g/l and the uranium content, from 1.5 ·
to $7.5 \cdot 10^{-7}$ g/l.

comparison of water samples collected over the productive dome of
hkapovsk structure and those collected outside of it shows that the
um content is higher over the petroleum deposit whereas the urani-
content is lower (Table 8). This is due, evidently, to the change in

Table 8

Within the oil-bearing zone			Outside of the oil-bearing zone		
No. of sample	Ra, g/l	U, g/l	No. of sample	Ra, g/l	U, g/l
16	$3.5 \cdot 10^{-12}$	$1.5 \cdot 10^{-7}$	9	$1.03 \cdot 10^{-13}$	$7.5 \cdot 10^{-7}$
17	$2.3 \cdot 10^{-12}$	$1.5 \cdot 10^{-7}$	15	$2.4 \cdot 10^{-13}$	$2.1 \cdot 10^{-7}$
18	$3.29 \cdot 10^{-12}$	$1.5 \cdot 10^{-7}$			

emical environment within the Shkapovsk structure where petro-
deposits and numerous oil seeps occur in a number of Devonian,
niferous and Permian horizons. The high content of CO_2 and CH_4
rocks over the petroleum deposit of the Shkapovsk structure
d also be noted. A correspondingly high content of the hydrocarbon
is indicated by the data of a water-gas survey [12].

SUMMARY

1. The ground waters of oil fields are characterized by similar radium contents irregardless of the stratigraphic, lithological or structural peculiarities of the region. All of the investigated waters of the sampled regions of geosynclinal, salt dome and platform type, as well as the fields located in reef complexes, have radium contents of the order of $n \cdot 10^{-10}$ g/l and rarely as low as 10^{-11} g/l. The uranium content of the waters is low, seldom exceeding $1.0 \cdot 10^{-7}$ g/l. In the upper water-bearing horizons of the oil fields the radium content in the water decreases to $n \cdot 10^{-12} - n \cdot 10^{-13}$ g/l. The uranium content increases to $n \cdot 10^{-5}$ g/l.

2. The maximum amount of radium is accumulated by ground waters of the calcium chloride type. The accumulation of radium is paralleled by increase in the $\dfrac{Cl-Na}{Mg}$ ratio (the coefficient of metamorphism) and is not always related to the mineral content. The maximum amount of uranium is accumulated by waters of the sodium carbonate type where uranium is present in the bicarbonate form which is well retained among the dissolved salts. The accumulation of uranium parallels the increase in the Na/Cl ratio, which characterizes the degree of freshening of natural waters.

3. In the oil fields the radium content in water increases as the oil pool is approached. As a rule the highest radioactivity is observed at the level of an oil pool and in the basal water-bearing horizons. The surface waters show, in some cases, an increase in radium content within the productive crests of structures and a decrease beyond the petroliferous area. A reciprocal relation is observed for uranium.

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THE DISTRIBUTION OF URANIUM IN THE MINERALS OF CALEDONIAN GRANITOIDS OF THE SUSAMYR BATHOLITH (CENTRAL TIEN SHAN)

L. L. Leonova and L. V. Tauson

V. I. Vernadskii Institute of Geochemistry and Analytical
Chemistry, Academy of Sciences USSR, Moscow

Abstract

The distribution of uranium in the minerals of granitoids of the Sussamyr
batholith has been studied. It has been established that this element is present
in all the minerals of the rocks but in different amounts. 40-50% of the uranium
in the rock is usually found in rock-forming minerals and 50-60% in accessory
minerals.

Microradiographic analysis and leaching of uranium from rocks show that
uranium is present in two forms: a) as an isomorphous constituent in accessory
minerals (zircon, sphene, allanite), b) as nonisomorphous, molecularly dissemi-
nated uranium in rock-forming minerals and microscopic and submicroscopic
inclusions of uranium minerals. Among the accessory minerals a specific ura-
nium concentrator typifies each of the intrusive phases.

In connection with the broad studies of the geochemistry of individual
elements and of uranium among them, more investigators are becoming
interested in the problem of the quantitative distribution and behavior of
this element in igneous rocks. Such investigations have acquired prac-
tical interest because igneous rocks as such may be regarded as poten-
tial sources of uranium [1, 2]. However, the basic problem of the geo-
chemistry of uranium in the magmatic stage is the elucidation of its
behavior during differentiation and emplacement of igneous bodies, the
regularities of its distribution during the process of crystallization, and
the conditions leading to its concentration in the pegmatitic and hydro-
thermal stages.

In studying the distribution of uranium during differentiation, most
investigators come to the conclusion that uranium has a tendency to be
concentrated in acid rocks [5, 6]. This is true for different chemical
rock groups, as shown by the increase of uranium content from gabbro
to granite, and for the successive differentiates in individual acid mag-
matic chambers.

There are still very few data in the literature on the distribution of
uranium in rock-forming minerals. In some cases they are contradic-
tory and do not point out the regularities in the behavior of uranium
during the crystallization of rocks. Some investigators [5, 6] believe
that almost all uranium is to be found in the accessory minerals

whereas others [2, 3, 7, 8] ascribe an important role to the non-diadochic uranium present in the essential rock-forming minerals.

We have undertaken a study of the behavior of uranium during the course of differentiation and crystallization in a large magmatic chamber using a well differentiated acid intrusive of Caledonian age.

The data on the distribution of uranium in the granitoids of the Susamyr batholith have already been published [9] and are presented in a generalized form with some additions in Table 1. They show that uranium is accumulated not in acid rocks in general but in the late acid differentiates of granitoid magmas.

Table 1. Distribution of Uranium in the
Susamyr Batholith Granitoids

	Intrusive phase	Amount of samples analyzed	Range of uranium content $n \cdot 10^{-4}$ %	Average uranium content $n \cdot 10^{-4}$ %
Main intrusive complex	Gabbro-diorites and diorites of the first phase ($\gamma_{K_1}^I$)	13	1.0—3.2	1.9
	Granodiorites and granites of the second (main) phaze ($\gamma_{K_2}^I$)	172	2.5—5.2	3.3
	Leucocratic granites ($\gamma_{K_3}^I$)	29	4.1—7.9	5.7
	Aplite dikes	26	7.1—8.4	7.6
?	Coarse-grained biotite granites of the Boorteke-Kavak type (γ_K^{II})	21	1.6—2.2	1.7

The granites of the Boorteke-Kavak type which do not enter into the main intrusive complex of the Susamyr batholith approach leucocratic granites ($\gamma_{K_3}^I$) in their acidity but have only half the uranium content of the more basic rocks of the main phase. The data for the Susamyr batholith, on the other hand, show a very significant (fourfold) uranium enrichment in the late acid differentiates.

The main problem of the present research was the study of the character and regularities of distribution of uranium among the rock-forming minerals.

During the course of our investigation we studied the distribution of uranium in the most widespread granitoids of the intrusive phases: in three samples of granitoids of the second (main) phase ($\gamma_{K_2}^I$), in one sample of leucocratic granite ($\gamma_{K_3}^I$) and in two samples of equigranular

...nites of the Boorteke-Kavak type ($\gamma_{k_3}^{II}$). Besides this, we analyzed ...nomineralic fractions from other samples for uranium. The miner-...gical composition of the rocks was calculated on large thin sections (x 9 cm^2), which permitted a much greater accuracy in the determin-...on of the content of accessory minerals. The samples of rocks and ...nerals were analyzed by the method described by one of the authors ...].

...The determinations of uranium in accessory minerals were made by ...ing small samples (1-20 mg) with KHF$_2$ and NaF and measuring the ...minescence with the fluorometer FM-42. The distribution of uranium ...he minerals of granitoids is shown in Table 2. Each figure is an ...rage of 3 to 4 analyses.

...Our investigation showed that uranium occurs in all minerals of the ...lyzed rocks. This is a very characteristic property of uranium, ...tinguishing it from many rare and ore minerals (Pb, Zn, Ta etc.) ...ch are usually concentrated in 2 or 3 minerals of the rock [11]. ...artz, potassium, feldspar, and plagioclase have the lowest uranium ...ntent, 0.3-1γ; zircon, allanite and the microscopic inclusions of ura-...m-thorium minerals of the uranothorite type have the highest ura-...m content.

...Typically, in all investigated rocks 40-50% of the total uranium is ...nd in the rock-forming minerals and 50-60% in the accessory min-...ls. Similar results were obtained by one of the authors for the ...nitoids of the Gornyi Altai [7].

...According to Larsen [3], in the Southern California batholith the bulk ...uranium is found in the essential minerals and only 10 to 30% in the ...essory minerals.

...A study of distribution of uranium in the minerals of the individual ...rusives has shown that the uranium content is definite for the miner-...l of each particular phase. For example, the zircons separated from ...i main intrusive phase ($\gamma_{k_2}^{I}$) contain on the average, 0.14% U (seven ...mples). The zircons from the leucocratic granites contain 0.3% U ...ir samples) and the zircons from granites (γ_{k}^{II}), 0.1% U (three sam-

...s). Characteristic for the rocks of each intrusive phase is the ura-...m content in sphene, allanite, and apatite.

...The identical distribution of uranium among the minerals over large ...as indicates that the average composition of the granitoids of a given ...se is the same and that the conditions of formation of each phase ...e nearly the same over large areas.

...As has already been pointed out, the rocks of the different intrusive ...ses differ in the distribution of uranium among the different acces-...ry minerals. It follows from the data of Table 2 that in the rocks of ...h intrusive phase one accessory mineral plays the leading role as ...carrier of uranium. In the granitoids of the main phase ($\gamma_{k_2}^{I}$) the

...n uranium concentrator is sphene. The presence of uranium in ...ene is probably due to the isomorphous substitution of uranium for

Table 2. Distribution of Uranium in the Susamyr
Batholith Granitoid Minerals

Mineral	Mineral content in rock, in weight %	Uranium content in mineral %	Amount of uranium in mineral converted to 1 g. of rock, γ	% of uranium in rock for any given mineral*	General uranium content in rocks γ/g
Porphyritic adamellite $-\gamma^I_{K_2}$ (S. ·ykamysh Range)					
Quartz	23.30	$1.5 \cdot 10^{-4}$	0.35	7	
Potassium feldspars and Plagioclase	68.00	$1 \cdot 10^{-4}$	0.67	13.4	
Biotite	8.30	$8 \cdot 10^{-4}$	0.66	13.3	
Hornblende	1.10	$5 \cdot 10^{-4}$	0.06	1.2	
Magnetite	0.32	$8 \cdot 10^{-4}$	0.03	0.6	
Zircon	0.014	$1.5 \cdot 10^{-1}$	0.21	4.2	
Sphene	0.47	$3.5 \cdot 10^{-2}$	1.65	33	
Allanite	0.11	$1.5 \cdot 10^{-2}$	0.17	3.4	
Apatite	0.04	$6.4 \cdot 10^{-3}$	0.03	0.6	
Total			3.83	76.5	5
Porphyritic tonalite $-\gamma^I_{K_2}$ (N. Kavak - Tau Range)					
Quartz	18.73	$3 \cdot 10^{-5}$	0.06	1.3	
Potassium feldspars and Plagioclase	68.46	$5 \cdot 10^{-5}$	0.34	7.6	
Biotite	10.58	$5 \cdot 10^{-4}$	0.53	11.8	
Hornblende	4.33	$4 \cdot 10^{-4}$	0.17	3.8	
Magnetite	0.10	—	—	—	
Zircon	0.027	$1 \cdot 10^{-1}$	0.27	6	
Sphene	0.52	$3 \cdot 10^{-2}$	1.66	37	
Allanite	0.09	$1.5 \cdot 10^{-2}$	0.14	3.1	
Apatite	0.09	$5.5 \cdot 10^{-3}$	0.05	1.1	
Total			3.22	71.5	4.5
Plagiogranite $-\gamma^I_{K_2}$ (Dzhumgol Range)					
Quartz	35.50	$1.4 \cdot 10^{-4}$	0.49	17.5	
Potassium feldspars and plagioclase	61.10	$1 \cdot 10^{-4}$	0.60	21.7	
Biotite	3.90	$1.5 \cdot 10^{-3}$	0.59	21.1	
Magnetite	0.74	$1.5 \cdot 10^{-3}$	0.11	3.9	
Zircon	0.014	$1.4 \cdot 10^{-1}$	0.20	7.1	
Sphene	0.30	$1.5 \cdot 10^{-2}$	0.45	16.1	
Allanite	0.04	$2 \cdot 10^{-2}$	0.08	2.9	
Apatite	0.04	$4.5 \cdot 10^{-3}$	0.02	0.7	
Total			2.49	90.7	2.8
Leucocratic granite $-\gamma^I_{K_8}$ (Dzhumgol Range)					
Quartz	33.70	$1 \cdot 10^{-4}$	0.34	8.1	
Potassium feldspars and plagioclase	63.80	$5 \cdot 10^{-5}$	0.34	8.1	
Biotite	2.76	$2.5 \cdot 10^{-3}$	0.70	16.7	
Magnetite	0.30	$1 \cdot 10^{-3}$	0.03	0.7	
Zircon	0.028	$2.5 \cdot 10^{-1}$	0.70	16.6	
Sphene	0,14	$2 \cdot 10^{-2}$	0.28	6.7	
Allanite	0.033	$4.1 \cdot 10^{-1}$	1.35	32.4	
Apatite	0.005	$2.4 \cdot 10^{-1}$	0.12	2.8	
Uranothorite		6			
Total			3.86	91.8	4.2

Table 2. (cont.)

Mineral	Mineral content in rock, in weight %	Uranium content in mineral, %	Amount of uranium in mineral converted to 1 g. of rock, γ	% of uranium in rock for any given mineral	General uranium content in rocks γ/g
Coarse-grained granite $-\gamma_K^{II}$ (N. Karak - Susamyr Range)					
Quartz	30.00	$3.5 \cdot 10^{-5}$	0.10	10	
Potassium feldspars and plagioclase	66.00	$2.5 \cdot 10^{-5}$	0.17	17	
Biotite	3.57	$5 \cdot 10^{-4}$	0.18	18	
Hornblende	0.98	$4 \cdot 10^{-4}$	0.04	4	
Magnetite	0.32	$8 \cdot 10^{-4}$	0.02	2	
Zircon	0.04	$1 \cdot 10^{-1}$	0.40	40	
Sphene	0.09	$1.7 \cdot 10^{-2}$	0.15	15	
Allanite	0.1	$5 \cdot 10^{-3}$	0.05	5	
Apatite	0.02	$3 \cdot 10^{-3}$	0.01	1	
Total			1.12	112	1
Coarse-grained granite - γ_K^{II} (N. Karak - Tan Range)					
Quartz	34.30	$3.5 \cdot 10^{-5}$	0.12	8	
Potassium felspars and plagioclase	61.70	$2.2 \cdot 10^{-5}$	0.14	9.3	
Biotite	2.70	$5 \cdot 10^{-4}$	0.14	9.3	
Hornblende	1.80	$4.2 \cdot 10^{-4}$	0.08	5.3	
Magnetite	0.24	$4 \cdot 10^{-4}$	01	0.6	
Zircon	0.03	$1 \cdot 10^{-1}$	0.3	20	
Sphene	0.11	$1.7 \cdot 10^{-2}$	0.19	12.6	
Allanite	0.16	$2.4 \cdot 10^{-2}$	0.38	25.3	
Apatite	0.014	$3 \cdot 10^{-3}$	0.004	0.25	
Total			1.34	90.6	1.5

*% of uranium for a given mineral, calculated on the basis of general uranium content in the rock.

...ium and to a less extent, for zirconium, as both of these elements ...present in sphene in considerable amounts. The absolute amount ...phene in the rocks of the main phase varies considerably, but the ...nium content in it is constant (300 γ/g of the mineral according to ...samples). Because of this, sphene, depending on the absolute ...ount in the given variety of granitoid, accounts for 20 to 37% of ura-...n in the rock.

...t follows from this that in the rocks containing sphene, allanite, or ...on as an accessory, sphene will control the distribution of uranium ...ong them. In the leucocratic granites ($\gamma_{k_3}^I$), however, the main con-

...trator of uranium is allanite (uranium content up to 0.4%), which ...ains 33% of all uranium in the rock. The presence of uranium in ...nite is explained apparently by isomorphous substitution of uranium ...horium and, in part, yttrium.

...n the granites of the Boorteke-Kavak type the main concentrator of

uranium is zircon. These granites are distinguished on the one hand by a rather high content of zircon (0.03-0.04% of the rock) and on the other by a very low total uranium content (1 - 1.5 γ/g of the rock). At the same time zircons in these granites are substantially enriched in uranium (0.1%) and account for 20 to 40% of its amount in the rock. Thus, the example of the Susamyr batholith granitoids shows that zircon is the main carrier of uranium only in those cases in which the rock has a low uranium content and a high zircon content. Moreover, the leucocratic granites ($\gamma^I_{k_3}$) are characterized by the presence of highly radioactive minerals of the uranothorite type and of submicroscopic inclusions of uranium and uranium-thorium minerals, probably oxides. These minerals are present in the granitoids of the main phase also, but in much smaller amounts.

Thus, the rocks of the different intrusive phases differ from each other not only in the total uranium content but in the character of its distribution among the minerals.

This quantitative study of the distribution of uranium in the minerals of the rocks does not completely answer the question of the form of its occurrence in the rocks. In investigating the form of occurrence of uranium in rocks, the authors resorted to autoradiography and differential leaching of uranium from rocks and minerals. The autoradiographic studies were made on the thick-emulsion plates of the AII NIKFI type with exposures of 4 to 48 days. Besides the autoradiographic method, the method of leaching of rocks and minerals with weak solvents was also used (5% solution of $(NH_4)_2 CO_3$ and 0.5% HCl).

The autoradiographic analysis of rocks and minerals showed that the occurrences of radioactive elements in the rocks may be divided into three groups. To the first group belong dispersed inclusions of radioactive elements giving widely separated individual tracks whose density in general is proportional to the uranium content of the rock or mineral. To the second group belong some accessory minerals with high uranium concentration. These minerals are characterized by a greater density of tracks which are distributed through the area of the mineral rather irregularly and yet not entirely without order. To the third group belong inclusions of uranium and uranium-thorium minerals which appear on autoradiographs as point sources of tracks or as small inclusions with high density of tracks. The autoradiographs of these three groups are presented in Figures 1, 2, 3 and 4.

In the first group individual tracks (from 5 to 50 tracks in the microscope field with magnification of 320) usually spread from grains of quartz, potassium feldspar, or plagioclase (Fig. 1).

The entry of uranium into the crystal lattices of quartz, potassium feldspar, or plagioclase is very improbable. It has been suggested that uranium occurs in these minerals in the inclusions of uranium minerals or of uranium-bearing accessory minerals such as zircon. The uniformity of distribution of the tracks indicates that they are not due to numerous submicroscopic inclusions of radioactive minerals. On the other hand, uranium present in these minerals is usually leached out by the HCl + H_2O_2 mixture and cannot therefore be inclusions of zircon.
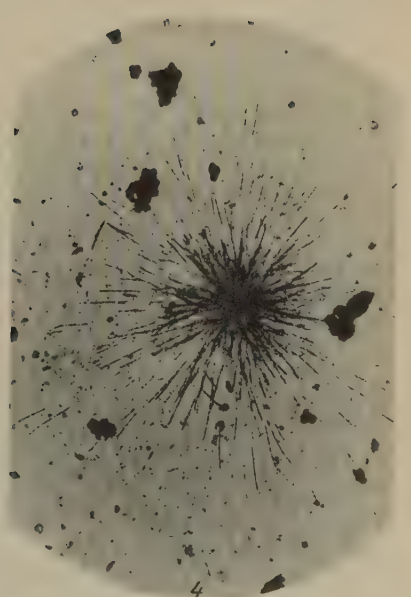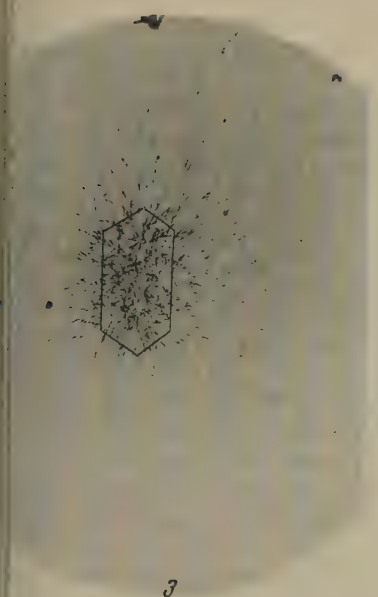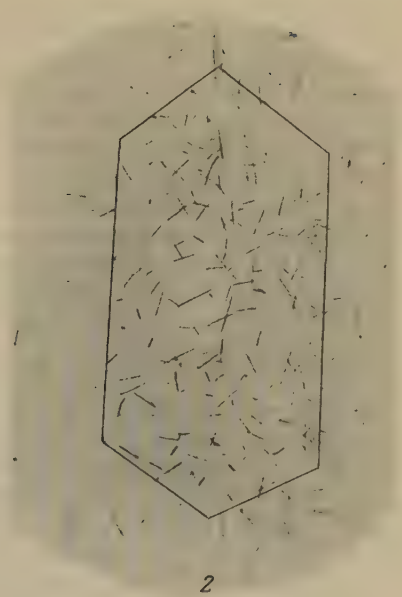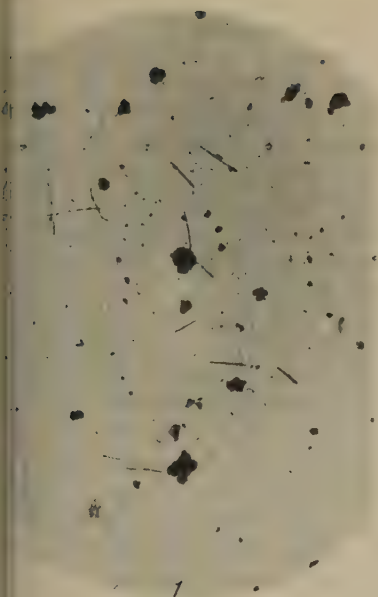
Fig. 1. Sample 7 T. Quartz, 48 day exposure (x320)
Fig. 2. Sample 1209. Zircon, 12 day exposure (x320)
Fig. 3. Sample 7 T. Uranothorite, 4 day exposure (x160)
Fig. 4. Sample 7 T. Point source, 48 day exposure (x320)

Evidently uranium is present in quartz, potassium feldspar, and plagioclase in the form of molecular segregations, once discussed by Vernadskii [12]. It is impossible at present to be more definite about the mode of occurrence of uranium in these minerals. In the opinion of the majority of investigators, in quartz, potassium feldspar, and plagioclase, uranium is adsorbed on the growth planes, on lattice defects, and on grain surfaces.

As can be seen from the tabulation of uranium content in individual minerals (Table 2), biotite is one of the uranium concentrators. Usually from 15 to 20% of the uranium content of a rock is found in biotite. On the autoradiographs the areas corresponding to biotite show an increased density of tracks and the tracks have a rather regular distribution as in quartz and feldspars. If biotite contains inclusions of radioactive minerals (zircon etc.), the distribution of the tracks is somewhat different. Their concentrations show up on the autoradiographs as areas with even greater track density.

Some investigators believe that uranium in biotite is concentrated mainly in zircon inclusions usually present in this mineral. We discovered, however, that the amount of uranium associated with zircon in biotite accounts for only 10% of all uranium in biotite. Mineralogical calculations show that biotites contain only a small part of zircon present in the rock. At the same time, lists of uranium distribution show that all zircon crystals in a rock contain less uranium than biotite. In decomposing biotite with the $HCl + H_2O_2$ mixture, only part of the uranium (30%) is leached out from the zircon inclusions. Zircon itself is not decomposed by this mixture.

All these facts indicate that of the uranium found in biotites not more than 10% can be credited to the inclusions of zircon. The main mass of uranium is in biotite itself. The treatment of biotite with weak solvent (5% solution of $(NH_4)_2 CO_3$) extracts only a very small part of uranium (8%). The main mass of uranium is evidently strongly held in biotite. It is difficult at present to judge of the manner of occurrence of uranium in biotite. It is possible that sorption plays an important role, but the possibility of isomorphous substitution is not excluded. The probability of the latter is increased by the fact that biotite is capable of capturing a number of rare elements.

In the case of uranium-concentrating minerals (zircon, sphene, allanite), the autoradiographs reproduce their crystal outlines and the areas on the plates corresponding to these minerals show increased density of tracks (Fig. 2). The uniform distribution of the tracks in these areas indicates that uranium occurs here mainly as an isomorphous admixture.

It is interesting to note that the experiments in leaching of uranium from zircon showed that its presence cannot be ascribed to isomorphism with zirconium alone. The treatment of zircon with weak solvents gives almost no uranium. The treatment with concentrated HCl, however, extracts about 30% of uranium. It is well known that zircon not decomposed by hydrochloric acid and the uranium extracted in this case must play a different role in the structure of this mineral.

For the same exposure, the inclusions of uranium and uranium-thorium minerals give tracks ten times as dense as those given by the accessory minerals. A study of the autoradiographs of the granitoids disclosed the presence of a mineral of the uranothorite type. In addition to the uranium tracks, this mineral records characteristic long thorium tracks (Fig. 3). It was extracted from the thin section and identified by chemical, optical, and x-ray analyses.

The autoradiographs of rocks show also very strong point-sources of tracks due apparently to submicroscopic inclusions of uranium minerals (Fig. 4). It is very difficult at present to judge of the nature of these inclusions, but the high density of the tracks indicates that they must be minerals with a very high thorium and uranium content.

That uranium is present diadochically in zircon, allanite, sphene, and other accessory minerals and also forms inclusions of its own minerals is acknowledged by the majority of investigators. The origin and mode of occurrence of "leachable" uranium is debatable at present. As has been pointed out earlier, one of the authors showed the presence in the Altai granites of the so-called "extra-silicate" non-diadochic uranium [7]. This mode of occurrence of uranium has been established by leaching powdered rock with a 5% solution of $(NH_4)_2CO_3$ with added H_2O_2.

The ammonium carbonate solution alone extracts about 70% of the leachable uranium. The remaining 30% passes into solution only after addition of H_2O_2. It was natural to assume that the non-diadochic uranium is present in the powder as U^{6+} and partly as U^{4+} ions or in the form of a mineral containing both uranium ions. Some authors [8] consider the leachable uranium as a supergene product, others believe that it may be oxidized to U^{6+} as the result of autometamorphism of the rocks. It seems very probable, however, that uranium may be present in the primary rocks in both valence states just as Fe^{3+} and Fe^{2+}, whose presence in the primary crystallizing magma is undoubted.

The presence of easily leached uranium has been noted by many authors and, since its amount varies widely, its content is characteristic for a given type of rock. Leaching of the granitoids of the Susamyr batholith with a 5% solution of $(NH_4)_2CO_3$ gave a rather low content of non-diadochic uranium. The results of leaching are given in Table 3. The data on leaching agree well with the data on the distribution of uranium in minerals and the results of autoradiography given in Table In almost all of the Susamyr rocks the amount of uranium leached out by $(NH_4)_2CO_3$ is small, amounting to 10-30% or, on the average, to % of the total uranium content.

Besides the experiments in leaching of uranium from the rocks, it was leached also from individual minerals. In leaching of uranium from quartz, potassium feldspar, and plagioclase, the extraction amounted to 100% with a complete preservation of the crystal lattice of the "host" mineral. The results of all these investigations suggest that uranium is present in the granitoids of the Susamyr batholith in the following forms:

Table 3. Leaching of Uranium from the Susamyr Batholith

Description of rocks	Number of samples	Uranium content in rock, γ	Range of amount leached, %	Average of amount leached, %
Granites and granodiorites of the main phase ($\gamma_{K_2}^{I}$)	19	3.2	10 - 30	20
Leucocratic granites ($\gamma_{K_3}^{I}$)	9	5.7	15 - 33	27
Uniform, medium-grained granites (γ_{K}^{II})	3	1.7	15 - 30	21

1) As ions dispersed in such minerals as quartz, potash feldspar, plagioclase and, in part, in some other minerals.

2) As an isomorphous admixture in the accessory minerals (zircon, sphene, allanite, and others) and in some essential minerals (biotite).

3) As submicroscopic inclusions of uranium-thorium minerals of the uranothorite type and in uranium and thorium minerals of unknown composition.

In discussing the form of occurrence of uranium in granitoids it is necessary to consider two sides of the question. The separation of uranium occurring in rocks into diadochic and non-diadochic has a definite geochemical meaning for it distinguishes uranium strongly bound in the lattices of the minerals from that which is not bound and may easily migrate from the rocks under the action of specific natural or artificial solvents without the destruction of the lattices of the essential or accessory minerals. On the other hand, the question of the mineralogical character of the inclusions with non-diadochic uranium is very important. They may apparently be of different kinds. This is indicated not only by our data but also by the data of other authors. It is known, for example, that Neuerberg [2] distinguishes six modes of uranium occurrence in rocks and in only one of these is uranium diadochic. In a determination of the mineralogical character of inclusions with non-diadochic uranium the size of the inclusions is very important. The study of the distribution of uranium in the minerals of the Susamyr granitoids suggests that microscopic and submicroscopic inclusions of uranium minerals in rocks and the dispersed uranium ions in the rock-forming minerals may be considered as a single series of uranium mineral segregations of different sizes.

SUMMARY

A number of conclusions can be drawn from an examination of the distribution of uranium in the minerals of the rocks of the Susamyr batholith.

(d) Uranium is present in all minerals of the rocks but in different amounts. Its content in the essential minerals is usually 40-50% of the total uranium content in the rock, in the accessory minerals, it is 50-...

In quartz and the feldspars uranium is non-diadochic, it occurs apparently in the intercrystalline spaces of these minerals and is easily leached out. The highest concentration of uranium is found in biotite. The mode of its occurrence in this mineral is not yet known, but there is no doubt that the greater part of it is in the biotite itself rather than in the inclusions of accessory minerals so frequently found in biotite. Among the accessory minerals of the investigated granitoids the highest concentration of uranium is found in zircon and allanite. Sphene has lower uranium content. However, because of its abundance, sphene is frequently the main carrier of uranium. Even in the rocks of average uranium content there are inclusions of uranium-thorium minerals. They do not, however, play an important role in the balance of uranium.

The investigation of the distribution of uranium in the rock-forming minerals showed that the rocks of each intrusive phase are characterized by different accessory minerals, which carry uranium. In the rocks of the main intrusive phase the principal uranium concentrator is sphene which usually holds 30-40% of the total uranium present in the rock. In the leucocratic granites the main carrier of uranium is allanite and in the granites of the Boorteke-Kavak type, zircon.

The distribution of uranium among the accessory minerals is determined basically by its total content in the magma, the content and distribution of the elements for which it has crystallo-chemical affinity, and the order of crystallization of the accessory minerals. The identity of these regulating factors for the rocks of a given phase leads to a definite distribution of uranium among the accessory minerals of that phase. In igneous rocks uranium has crystallo-chemical affinity for calcium, thorium, and zirconium.

An analysis of the distribution of uranium among rock-forming minerals during crystallization shows that the most characteristic feature in the behavior of uranium during this process is its accumulation in the rest magma. During the early stages of crystallization some of the uranium is non-diadochically captured by the rock-forming minerals but in general the rest magma is greatly enriched in it. In the later stages of crystallization the first signs of the affinity of uranium for calcium, thorium, and zirconium become apparent and uranium is captured by the accessory minerals crystallizing at this stage. However, in spite of the capture of uranium by the accessory minerals the process of its concentration in the rest magma continues when the volume of the melt is sharply reduced. Finally, in the concluding stages of crystallization uranium is precipitated in the non-diadochic form (inclusions of uranium and uranium-thorium minerals).

The property of uranium to accumulate in the acid rest magmas during crystallization is evidently intimately related with the general

geochemical pattern of its behavior which is manifested in its concentration in the acid differentiates of magmatic chambers.

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BORON ISOMORPHISM IN SILICATES

V. L. Barsukov

V. I. Vernadskii Institute of Geochemistry and Analytical
Chemistry, Academy of Sciences USSR, Moscow

Abstract

different character of interdependence of boron and aluminum isomorphism
silicon in silicates belonging to different structural groups has been estab-
    Some kinds of boron isomorphism in silicates are considered. Each of
is typical for a definite group. It has been shown that the boron isomor-
    may occur only in orthosilicates, metasilicates with a chain radical and in
frame silicates, whereas in most framework silicates as well as in double
and sheet silicates this isomorphism is scarcely probable. After having
    ied the possibilities for the isomorphism in various rock-forming minerals
    usive rocks, the conclusion is drawn that the boron-content of these rocks
    nected with an increased boron concentration in plagioclases.

e isomorphism of boron in silicates is one of the still little studied
mena in crystal chemistry. However, there are sufficient data on
bject at present to permit a preliminary generalization. The high
rature of formation and the complexity of the crystal lattices al-
great variety of different isomorphous substitutions in the silicate
ures.

th the boron-oxygen tetrahedron (edge $\sim$ 2.4 Å) and the aluminum-
n tetrahedron (edge $\sim$ 2.8 Å) are comparable in size to the silicon-
n tetrahedron (edge $\sim$ 2.61 Å). This fact, together with the equal-
valence of the boron and aluminum ions, makes it possible for
f them to replace silicon simultaneously in a number of silicate
ures. This does not cause any great strain in the crystal lattice,
se the sum of the tetrahedral edges of B^{3+} and Al^{3+} is twice the
f the Si^{4+} tetrahedron. But on the other hand, since a boron ion is
r than the silicon ion by approximately the same amount by which
minum ion is larger than the silicon ion, there is a considerable
nce in the behavior of these ions in isomorphism in different sili-
tructures. The difference in the size of the B^{3+} and Al^{3+} ions
sts itself in the fact that boron appears in the lattice in the four-
ordination only, whereas aluminum may have either fourfold or
coordination. Boron isomorphism in silicates depends first of
the position of the silicon ions in the structure and on the pres-
nd position of aluminum ions. These positions are constant char-
stics of different silicate structures. Therefore, a discussion of
nt types of boron isomorphism in the silicates is best carried out
tely for each of the silicate structure groups.

V. L. BARSUKOV

The orthosilicates are nearest to the closest packed structure, and their crystal lattices are built mainly of independent $[SiO_4]^{4-}$ tetradedra or of doubled tetradedra $[Si_2O_7]^{6-}$. It was shown by Belov [1, 2] that the construction of a crystal lattice on the principle of closest packing is possible only if the ratio of the cation and anion radii does not exceed 0.22 in the case of tetradedra and 0.41 in the case of octahedra, i.e., if this ratio corresponds to the lowest limit of stability for the given coordination number. The ratio of the radii of boron and oxygen is 0.15; of aluminum and oxygen, 0.43; and hence, in lattices built on the principle of closest packing, boron can have only fourfold coordination, and aluminum, only sixfold coordination. This explains the fact that in orthosilicates the substitution of aluminum for silicon is practically unknown, whereas the replacement of Si^{4+} by B^{3+} is possible.

It is known that the substitution of the $[AlO_4]^{5-}$ tetradedra for the $[SiO_4]^{4-}$ tetradedra in the silicates is accompanied by the simultaneous entry into the lattice of relatively large cations with low charge (Na^{1+}, K^{1+}, Ca^{2+}, etc.) which compensate for both volume and electrostatic charge. The replacement of the $[SiO_4]^{4-}$ tetradedron by the $[BO_4]^{5-}$ tetradedron, on the other hand, must be accompanied, for the same reasons, by the introduction among the cations of a small cation with a charge one unit higher than the charge of the cation bound to the $[SiO_4]^{4-}$ tetradedron. This can be illustrated by comparison of the minerals sinhalite and olivine. It was stated by Larsen [3] that sinhalite can be regarded as olivine in which silicon is replaced by boron, and one magnesium ion by aluminum: olivine, $MgMgSiO_4$; sinhalite, $MgAlBO_4$. This example confirms the statement above about one means of compensation when silicon is replaced by boron. But this occurs only if all silicon is replaced by boron and one half of the magnesium octahedra are replaced by aluminum octahedra, and results in the formation of a new mineral species, an independent boron mineral.

These two isostructural compounds are not miscible, because of the impossibility of isomorphism between magnesium and aluminum without which there can be no compensation for the replacement of silicon by boron.

There is a mention in the literature [2] of isomorphism between magnesium and aluminum in spinel. It is believed that such isomorphism may occur also in ino- and phyllosilicates (micas, hornblendes, etc.), in which magnesium and aluminum are not actually completely miscible but are only supposed to be at the melting temperature. However, the lattice structure of these minerals is much farther from the closest packed type than that of olivine, and the possibility of isomorphism in them is much greater. It may be objected that spinel has a lattice very near the closest packed type, yet this isomorphism occurs in it anyway. But there is a difference between the structure of olivine and spinel which cannot be neglected. In olivine the structure is composed of magnesium octahedra, and the bands of octahedral spaces are occupied by silicon tetrahedra, but in spinel the basic pattern is that of aluminum octahedra and the bands of octahedral spaces are occupied

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magnesium tetradedra [1]. In spinel aluminum octahedra replace
magnesium tetradedra, but in olivine they cannot replace magnesium
octahedra because the octahedra of magnesium and aluminum differ in
size by about 10%. However, in passing from octahedral to tetrahedral
coordination, the distances between the ions are reduced by 6 to 8% [4],
and therefore the edge of a magnesium tetradedron becomes almost
equal to the edge of an aluminum octahedron, and so they can be iso-
morphous in spinel but not in olivine.

The volume and charge compensation in the replacement of silicon
by boron may be fulfilled also by the entry of additional cations or by
an increase in the number of trivalent ions in sixfold coordination.

It is known [1, 2] that, in the case of closest packing in the structure
of the infinitely extended type, the number of octahedral spaces equals
the number of anions. Inasmuch as the ratio of the number of cations
to the number of anions is always less than 1:1, some of the octahedral
sites are always vacant.

In heterovalent isomorphism, the compensation is very easily
achieved by the entry of additional cations if the ionic radius of the in-
coming cation is such that the vacant octahedral (or tetrahedral) spaces
in the lattice can be occupied. Therefore, the most probable means of
compensation in this case is the increase in the number of cations with
sixfold coordination.

It is possible that this is the method of compensation in the replace-
ment of silicon by boron in garnets. If the formulas of sinhalite and
garnet are compared, it will be seen that they differ by the number of
cations in the sixfold coordination:

$$\text{sinhalite ----- } Mg_3\,Al_3\,[BO_4]_3$$

$$\text{garnet ------- } Mg_3\,Al_2\,[SiO_4]_3$$
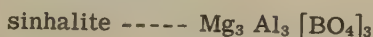
It must be mentioned that this method of compensation in hetero-
valent isomorphism is rather rare.

The third, the most interesting and apparently most widespread,
method of silicon-boron isomorphism does not require any compensa-
tion. The $[SiO_4]^{4-}$ tetrahedron may be replaced by the $[BO_3(OH)]^{4-}$ tet-
rahedron, as for example in datolite. Another example of such substi-
tution is dumortierite, if its chemical composition and structure are
regarded as derived from sillimanite:

$$Al_8[SiO_4]_4\,[SiO_4]$$

$$Al_8[SiO_4]_4\,[BO_3OH]$$
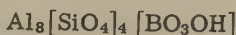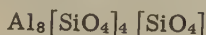
It is this type of isomorphism which probably explains the high con-
tent of boron in some garnets.

Two samples of andradite from the Turinsk locality in the Urals*,
B_2O_3 content was found to be 0.16 and 0.30%**. According to

Bertolani [6], in some of the garnets from Arendal the B_2O_3 content reaches 1.5%.

An analysis of one of the specimens of andradite is given in Table 1.

In the substitution of the $[SiO_4]^{4-}$ tetradedron by the $[BO_3OH]^{4-}$ tetrahedron, the number of boron and silicon atoms must be equal. It is not difficult to calculate that for this condition to be fulfilled the B_2O_3 content must be twice the H_2O content (wt. %). The content of boron and water fulfill this condition exactly. It may be assumed, therefore, that the most probable mechanism of boron isomorphism in the orthosilicates is the replacement of the $[SiO_4]^{4-}$ tetrahedron by the $[BO_3OH]^{4-}$ tetrahedron.

These considerations are in agreement with the hypothesis presented earlier [7], that during epidotization of garnets boron may go into solution and datolite may form, whose structure also includes the $[BO_3OH]^{4-}$ group.

Table 1

SiO	36.44
B_2O_3	0.30
Fe_2O_3	30.47
CaO	31.00
MgO	1.77
$+H_2O$	0.17
$-H_2O$	0.10
	100.25

In the metasilicates with the chain radical, the possibilities for isomorphous substitutions in the radical are greater because this group of silicates is farther in its structure from the closest packing type than are the orthosilicates.

In the chain radical the most favorable and therefore most probable is the simultaneous replacement of the silicon tetrahedra by the aluminum and boron tetrahedra. In this case the general geometry and the integrity of the $[SiO_4]^{4-}$ chain are not destroyed.

The Si--O distance in the silicates is usually 1.60 to 1.65 Å, the B--O distance is from 1.45 to 1.50 Å, and the Al--O distance is from 1.70 to 1.80 Å. The sum of the interionic distances B—O and Al—O is twice the interionic distance (Si--O), or 3.20 Å. But since in this substitution the length of the chain increases (by replacement of a part of $[SiO_4]^{4-}$ by $[AlO_4]^{5-}$), it must result in a simultaneous entry among the cations of some small ions with the charge one unit less than that of the ions attached to the silicon tetrahedra. This may be illustrated by hypersthene and kornerupine:

Hypersthene -- $(Mg, Fe)_2 [Si_2O_6]$, B_2O_3 from 0.0 to 0.02%

Kornerupine -- $(Mg, Al)_2 [(Al, Si)_2O_6]$, B_2O_3 up to 3.6%.

This mechanism of isomorphous substitution of boron in the metasilicates with chain structure is possible only if the chains of tetrahedra are independent. When they become united and form bands or sheets, the conditions for the preservation of the chain radical can no longer be fulfilled in this type of isomorphism. In both cases Al^{3+} partially replaced Si^{4+}, but, as a rule, with a strictly defined ratio of silicon and aluminum.

For example, in the double chain silicates, one quarter of the silicon ions may be replaced by aluminum, but one quarter only, for only then

the infinite band structure be built. In the sheet radicals, either
a quarter or one half of the silicon ions can be replaced by aluminum,
the ratio of aluminum and silicon must be exactly one quarter or
one half for only then can the infinite sheets be built.

This is really not isomorphism of Si^{4+} and Al^{3+}, for the very concept
of isomorphism implies all possible ratios of Si^{4+} and Al^{3+}, but forma-
tion of independent aluminosilicate radicals. The same reasons show
the impossibility of isomorphism between Si^{4+} and B^{3+} in these silicates
but theoretical possibility of formation of independent silicate radicals
of the same type as the aluminosilicate radicals. A boro-fluosilicate of
phlogopite composition, $KMg_3 [BSi_3O_{10}]F_2$, has recently been synthe-
sized [8]. In nature, however, considering the difference in the abun-
dance of aluminum and boron, the formation of independent borosilicates
of the double chain or sheet type is very improbable.

In confirmation of what has been said, Table 2 presents the results
of analysis of some double chain and sheet silicates for their B_2O_3 con-
tent.*

Most of the tectosilicates, like the minerals of the preceding two
structure groups, have a constant ratio of silicon and aluminum in each
compound. They also must be regarded as compounds with definite in-
dependent aluminosilicate radicals. Therefore, the conclusion that the
silicon-boron isomorphism is impossible or improbable is as true for
tectosilicates as for the two preceding silicate group. But there are
three groups of minerals among the tectosilicates which hold a very
special position; these are the plagioclases, the scapolites and the po-
tassium-barite feldspars. In these minerals the ratio of aluminum and
silicon varies from one quarter to one half; i.e., they exhibit partial
isomorphism of silicon and aluminum limited by the possible compensa-
tion.

It would seem that such limited type of isomorphism in these miner-
als might be expected of boron also. However, the peculiarities of the
silicate structure lead to boron isomorphism which is quite differ-
ent from that in the cases already discussed.

Table 2

Hornblende	Phlogopite	Biotite	Comments
0.003	0.000	—	From magnetite - ludwigite scarns
0.006	0.005	—	of the southern Yakutiya formation
0.009	0.002	—	
0.000	—	0.000	From Trans-Baikal and Gornaya
0.000	—	0.000	Shoriya granitoids
0.003	—	—	
0.005	0.0005	0.0005	From data by Goldshmidt and
			Peters [9]

analyses were made by E. N. Savina in the spectrographic laboratory of the
Institute of Geochemistry and Analytical Chemistry.

In tectosilicates, in contradistinction to all other groups, each oxygen ion in a silicon-oxygen tetrahedron is shared between two neighboring tetrahedra; i.e., all vertices of the tetrahedra are united to each other. The negative charge is acquired by the structure when some of the silicon-oxygen tetrahedra are replaced by aluminum-oxygen tetrahedra. The cations (and in some minerals water molecules) are distributed in the spaces and channels within the three-dimensional structure and neutralize its charge.

With this lattice structure aluminum- and boron-oxygen tetrahedra will be subjected to tension by the polarizing effect of the surrounding silicon ions, which are much stronger polarizers than the B^{3+} and Al^{3+} ions. The possibility of such stretching of the aluminum- and boron-oxygen tetrahedra by silicon can be seen from a comparison of the bonding forces and energies within these tetrahedra (Table 3).

Therefore, the boron-oxygen tetrahedra in tectosilicates will be larger than in other silicate structures; they will be larger than the silicon-oxygen tetrahedra and approach the size of the aluminum-oxygen tetrahedra. The aluminum-oxygen tetrahedron, because of its size, which exceeds that of the silicon-oxygen tetrahedron, will not change its dimensions substantially under the effect of polarization, because in this case, simultaneously with the polarizing action of the nearest silicon ions, the antipolarization effect of the more remote silicon-oxygen tetrahedra will be felt. Indeed, the size of aluminum-oxygen tetrahedra in the aluminum tectosilicates is almost the same as in other silicate groups and is about 2.8 Å on the edge, while the edge of the boron-oxygen tetrahedron in datolite is 2.45 Å and in danburite, as much as 2.7−2.8 Å [10, 11].

Table 3

	Binding force	Binding energy*
Si−O	1.00	32.5
Al−O	0.75	22.4
B−O	0.75	25.3

*The binding energy is calculated in electron-volts, according to A. E. Fersman.

Thus, in connection with tectosilicates it is more correct to speak of isomorphism between aluminum and boron rather than between boron and silicon, and of the possibility of complete replacement of aluminum by boron. To illustrate this, the following minerals can be used:

Analcime — Na [AlSi$_2$O$_5$] H$_2$O

Searlesite — Na [BSi$_2$O$_6$] H$_2$O

Albite — Na [AlSi$_3$O$_8$] −− Ca [Al$_2$Si$_2$O$_8$] — Anorthite

Reedmergnerite −− Na [BSi$_3$O$_8$] −− Ca [B$_2$Si$_2$O$_8$] −− Danburite
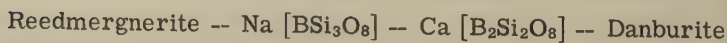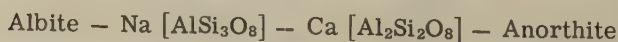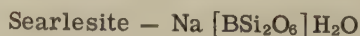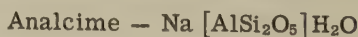
Of especial interest is the comparison of the plagioclase group with the reedmergnerite-danburite series. It follows from the preceding that boron must accumulate in minerals with partial Si^{4+} − Al^{3+} isomorphism. On the other hand, the greater the number of Si^{4+} ions

ⁱⁱaced by Al^{3+}, the greater the possibility of the replacement of alu-
ᵐⁱnm by boron in the lattice of the mineral. It follows that the more
ᵐᵃᶜ plagioclases should contain more boron (comparing, of course,
ᵖᵘlagioclases formed in the same magmatic chamber).

The available data confirm this. According to Bertolani's data [6],
ᵃⁱoclase contains 0.006% B_2O_3 and labradorite, 0.063% B_2O_3. Getling
ⁱᵛSavina [12] have also checked the above hypothesis and found 0.018%
ᵐⁱ in andesine (An_{38}) and 0.030% B_2O_3 in labradorite (An_{52}) (the pla-
ᵍⁱlases were picked from a gabbro-diorite).

Of course this rule cannot be without exceptions, since many factors
ᵃᵈⁱᵗ the primary distribution of dispersed elements in intrusive rocks,
ⁱⁿ the overwhelming majority of cases we can expect an increase in
ᵐⁱn in the plagioclases as they become more basic. It is probably
ⁱᵃ fact that explains the higher clarke of boron in some basic rocks
ᵛⁱᵈ by Sahama [13], although his belief that the boron is concentrated
ᵃⁱrk minerals must be considered erroneous.

The present author believes that further, more profound, study of
ᵈⁱᵈistribution of boron in intermediate and basic rocks will shed light
ᵛⁱbnly on the crystal chemistry of boron in silicates but on other
ᵐⁱlems of the geochemistry of boron which may have practical im-
ᵃⁱance.

ⁱⁱ number of preliminary conclusions can be drawn from the mate-
ᵃᵗpresented here:

T. There is a definite relationship between the isomorphism of boron
ᵃⁿⁱaluminum with silicon, but the character of this relationship is dif-
ⁱⁱ nt in different silicate structures.

nⁱ. In orthosilicates the most probable type of boron isomorphism is
ⁱⁱⁱeplacement of the $[SiO_4]^{4-}$ tetrahedron by the $[BO_3(OH)]^{4-}$ tetra-
ⁱon, although the possibility of direct substitution of B^{3+} for Si^{4+}
ᵐⁱ compensation by the entry of additional ions in sixfold coordina-
ⁱⁱ is not excluded.

nⁱ. In metasilicates with chain radicals boron may enter into the lat-
ᵈⁱ if two silicon-oxygen tetrahedra are simultaneously replaced by
ⁱⁱetrahedra of boron and aluminum.

nⁱ. In tectosilicates, boron may isomorphously enter into the lattice
ⁱⁱ uly a limited number of minerals which have a variable silicon-
ᵃⁱⁱⁱⁱⁱinum ratio and in its character this isomorphism is nearer to the
ⁱᵘⁱtitution of Al^{3+} by B^{3+} than of Si^{4+} by B^{3+}.

nⁱ. In the rest of the tectosilicates and in ino- and phyllosilicates, the
ᵗⁱability of boron isomorphism is low, for it leads to the destruction
ⁱⁱe radicals.

Jⁱ. It follows from the considerations presented above that the boron
ⁱent in the intrusive rocks must depend on its content in the plagio-
ᶜⁱe feldspars, which increases as they become more basic, and on
ⁱⁱcontamination of the magma with boron.

ᵃⁱhese conclusions not only are important from the point of view of
ⁱtal chemistry, but they have genetic significance. They provide a

geochemical approach to such a complex problem as the genetic relationship between hypogene borate mineralization and intrusives and a whole series of other problems of the geochemistry of boron. But since these questions are beyond the scope of this paper, they will be discussed in a separate work.

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THE CHEMICAL COMPOSITION OF GALENA

Yu. S. Nesterova

Institute of Ore Deposits, Petrography, Mineralogy and
Geochemistry, Academy of Sciences USSR, Moscow

Abstract

Forty chemical analyses of galena from various areas of the USSR (24 by the
author) have been recalculated for mineral admixtures. It has been found that
the primary minerals, the following occur especially commonly as admixtures
in the galena under examination: argentite, boulangerite, sphalerite, chalcopyrite,
emplbuthinite, pyrite; of the secondary—cerussite, covellite and anglesite are
most frequently encountered. The rather common admixture of native sulfur re-
quires a special investigation and is a problem for further study.
The data obtained allow comparison of galena from these areas of the USSR
according to character and amount of inclusions of silver, antimony, bismuth and
other minerals. The author concludes that the elements commonly occurring in
galena—Ag, Bi, As, Sb, Sn, Cu and Fe—do not enter the galena lattice but belong
to independent minerals, a very fine admixture of which commonly may not be
detected under the microscope.

The formula of galena is very simple—PbS. Frequently, however, a
considerable number of elements enter into the chemical composition
of this mineral. Most commonly they are: silver, bismuth, antimony,
arsenic, copper, tin, and sometimes thallium.

Betekhtin [1] believes that "these elements, in most cases, occur as
microscopic inclusions of other minerals." However, a straightforward
demonstration of the mode of occurrence of these elements is lacking.
The usual reference to isomorphous substitution is not sufficiently con-
vincing and is not confirmed by x-ray analysis. Replacement of sulfur
in galena by selenium and tellurium has been definitely established and
it is known that galena, PbS (a_0 = 5.924 Å) is isomorphous with claus-
thalite, PbSe (a_0 = 6.162 Å) and with the high temperature modification
of α-matildite, AgBiS$_2$ (a_0 = 5.632 Å) for the pseudo-isometric cell) [2].
It is generally known also that galena often occurs in extremely fine-
grained mixtures with vein and country rock minerals. Crystals of
galena are frequently found in intimate intergrowth (in some cases ori-
ented) with many simple and complex sulfides and oxidized lead miner-
als. Commonly these admixtures, because of their minute size, cannot
be discovered either by the x-ray or mineralographic methods, and for
this reason spectrochemical and chemical analyses are of special im-
portance in the study of galena.

For this chemical study of galena the author collected forty com-
plete analyses of specimens from the deposits in the southeastern part

Table 1. Chemical Analyses of Galena

Elements	No. of sample							
	1	2	3	4	5	6	7	8
Pb	82.40	85.25	84.37	85.45	85.18	84.48	85.35	79.67
Ag	0.26	0.21	0.21	0.20	0.25	0.23	0.27	0.05
Cu	0.10	0.05	--	--	--	--	--	0.03
Fe	0.07	0.03	0.02	--	--	--	--	0.22
Zn	--	--	0.07	--	0.36	0.33	--	2.96
Cd	0.02	--	trace	--	--	--	--	0.02
Mn	--	--	--	--	--	--	--	--
As	--	--	--	--	--	--	--	--
Bi	--	--	0.001	--	--	--	--	trace
Sb	0.32	0.10	0.20	0.33	0.30	0.33	0.33	0.006
Sn	0.10	0.14	--	0.07	0.16	0.15	--	--
Te	--	trace	--	--	--	--	--	--
Se	--	--	--	--	--	--	--	--
S	13.02	13.31	13.16	13.48	13.67	13.62	13.54	14.09
SO_3	--	--	--	--	--	--	--	0.07
Au	--	--	--	--	--	--	--	--
CO_2	--	--	--	--	--	--	--	--
Al	--	0.10	--	--	--	--	--	--
SiO_2	0.45	0.02	0.05	0.46	0.16	0.30	0.40	2.96
Fe_2O_3	--	--	--	--	--	--	--	--
CaO	0.20	0.08	0.02	--	--	--	--	--
MgO	0.13	0.11	0.12	--	--	--	--	0.06
BaO	--	--	--	--	--	--	--	0.14
PbO ⎫ Computed	2.86	0.99	2.05	--	--	--	--	--
CO_2 ⎬	0.56	0.21	0.40	--	--	--	--	--
O ⎭	0.01	0.03	0.026	0.02	0.042	0.042	--	--
Total	100.50	100.63	100.70	100.01	100.12	99.48	99.89	100.28
Sp. Gravity	7.31	7.55	7.468	--	--	--	--	6.763
Analyst and year	Yu. S. Nesterova, 1952				P. N. Nisenbaum, 1957			

Elements	No. of sample							
	9	10	11	12	13	14	15	16
Pb	85.33	84.29	26.65	85.60	85.27	75.88	74.01	74.72
Ag	--	--	--	0.02	0.04	--	0.01	0.03
Cu	0.35	0.08	--	0.06	0.10	0.11	2.89	0.32
Fe	0.10	0.06	0.35	0.03	0.04	0.42	0.03	0.05
Zn	0.03	0.27	--	--	0.008	0.11	--	--
Cd	--	0.02	trace	--	--	--	--	--
Mn	trace	--	0.17	trace	--	--	--	--
As	--	--	0.47	--	--	--	--	--
Bi	0.003	trace	trace	trace	trace	--	--	--
Sb	trace	0.01	0.01	0.06	0.01	--	--	--
Sn	--	--	--	--	--	--	--	--
Te	--	--	--	--	--	--	--	--
Se	--	--	--	--	--	--	--	--
S	13.45	13.26	4.33	13.30	13.31	12.63	12.68	11.79
SO_3	--	0.03	0.25	--	0.05	2.83	2.38	3.52
Au	--	--	--	--	--	--	--	--
CO_2	--	--	1.21	--	--	--	--	--
Al	--	--	--	--	--	--	--	--
SiO_2	0.36	0.88	22.65	0.05	0.18	0.12	0.83	0.39
Fe_2O_3	--	--	18.80	--	--	--	--	--
CaO	0.25	0.31	21.84	0.11	0.19	0.05	0.04	--
MgO	0.16	0.16	0.77	0.19	0.09	0.09	--	--
BaO	0.01	0.05	0.06	--	0.09	--	0.04	--
PbO ⎫ Computed	0.02	0.44	2.25	0.80	0.13	7.89	6.15	9.81
CO_2 ⎬	0.004	0.088	--	0.16	0.026	--	--	--
O ⎭	--	--	--	--	--	--	--	--
Total	100.06	99.95	99.81	100.39	99.64	100.02	99.06	100.63
Sp. Gravity	7.460	--	--	--	7.439	--	--	--
Analyst and year	Yu. S. Nesterova, 1952							

Table 1. (cont.)   837

Elements	No. of sample							
	17	18	19	20	21	22	23	24
Pb	83.97	85.10	85.39	84.39	85.95	76.88	85.62	85.73
Ag	—	0.04	0.06	0.04	0.10	0.02	0.05	0.04
Cu	0.06	0.25	—	0.13	0.05	0.05	0.01	—
Fe	0.03	0.20	0.23	0.07	0.04	0.17	—	0.38
Zn	0.17	0.02	—	trace	trace	6.03	0.22	—
Cd	0.008	—	—	trace	trace	0.02	0.01	—
Mn	—	trace	—	—	—	—	—	—
As	—	—	—	—	—	—	trace	trace
Bi	trace	0.01	0.06	trace	trace	trace	—	—
Sb	0.01	0.04	0.04	—	0.006	0.03	0.02	0.03
Sn	—	—	—	—	—	—	—	—
Te	—	—	—	—	—	—	—	—
Se	—	—	—	—	—	—	—	—
S	13.12	13.43	13.34	13.15	13.36	14.92	13.28	13.28
SO_3	0.01	0.02	—	0.02	0.10	0.03	—	—
Au	—	—	—	—	—	—	—	—
CO_2	—	—	—	—	—	—	—	—
Al	—	—	—	—	—	—	—	—
SiO_2	0.15	0.82	0.52	1.63	0.19	0.29	0.36	0.75
Fe_2O_3	—	—	—	—	—	—	—	—
CaO	0.17	—	—	0.03	0.12	0.10	—	—
MgO	0.05	0.19	—	0.13	0.07	0.10	—	—
BaO	0.03	0.04	—	0.04	0.07	0.06	—	—
PbO ⎫ Com-	2.34	—	—	0.71	—	0.94	0.04	0.09
CO_2 ⎬ puted	0.46	—	—	0.14	—	0.185	0.01	0.018
O ⎭	—	—	0.06	—	—	0.053	0.09	0.163
Total	100.58	100.18	99.70	100.48	100.06	99.88	99.71	100.48
Sp. gravity	7.825	7.333	7.42	7.292	7.51	6.910	—	—
Analyst and year	Yu. S. Nesterova, 1952							

Elements	No. of sample							
	25	26	27	28	29	30	31	32
Pb	85.92	86.45	52.50	85.95	84.44	82.04	84.86	81.93
Ag	0.01	0.04	--	0.15	0.24	0.15	0.21	0.37
Cu	—	0.03	1.54	—	--	—	—	0.26
Fe	0.17	0.10	0.15	--	--	0.78	—	--
Zn	0.01	0.02	0.02	--	--	—	—	trace
Cd	—	—	—	—	--	--	—	—
Mn	trace	—	trace	—	--	—	—	—
As	—	—	—	--	0.39	1.68	1.07	3.45
Sb	—	0.02	--	--	—	—	—	—
Sn	—	—	—	—	—	--	--	—
Te	—	—	—	--	--	—	—	—
Se	—	—	—	--	—	--	—	—
S	13.30	13.48	9.25	13.44	13.19	13.77	13.87	13.49
SO_3	—	—	9.81	--	—	—	--	—
Au	—	—	—	—	—	—	—	—
CO_2	—	—	--	--	—	—	—	—
Al	—	—	—	--	--	--	—	—
SiO_2	0.36	0.33	0.98	0.56	0.32	0.32	0.40	0.55
Fe_2O_3	—	—	—	—	--	—	--	—
CaO	—	—	0.12	--	—	—	—	—
MgO	—	—	0.14	—	--	--	—	—
BaO	—	—	2.82	—	—	—	—	—
PbO ⎫ Com-	0.38	—	22.77	—	2.03	—	—	0.40
CO_2 ⎬ puted	0.075	—	—	—	0.40	—	—	0.08
O ⎭	0.072	—	—	--	—	--	—	—
Total	100.30	100.47	100.10	100.10	101.01	99.64	100.41	100.53
Sp. gravity	—	—	—	—	—	—	—	--
Analyst and year	Yu. S. Nesterova 1952			P. N. Nisenbaum 1955				

Table 1. (cont.)

Elements	No. of sample							
	33	34	35	36	37	38	39	40
Pb	84.08	80.75	86.22	85.94	85.80	85.92	86.22	83.73
Ag	0.15	1.39	0.12	0.12	0.23	0.12	--	- -
Cu	--	--	trace	trace	trace	--	--	0.06
Fe	0.35	--	0.01	0.03	0.03	--	--	0.42
Zn	--	--	--	--	--	--	trace	trace
Cd	--	--	--	--	--	--	--	--
Mn	--	--	--	trace	trace	--	--	--
As	--	--	--	--	--	--	--	0.41
Bi	0.99	3.93	0.06	0.22	0.06	0.001	--	trace
Sb	--	--	--	0.15	0.02	--	0.08	0.17
Sn	--	--	--	--	--	--	--	--
Te	--	0.41	--	--	--	--	--	--
Se	--	trace	--	--	--	--	--	--
S	13.66	13.58	13.96	13.96	13.87	13.83	13.37	13.30
SO₃	--	--	--	--	--	--	--	--
Au	--	--	--	--	--	trace	--	--
CO₂	--	--	--	--	--	--	--	--
Al	--	--	--	--	--	--	--	--
SiO₂	0.05	--	---	--	--	--	--	0.33
Fe₂O₃	--	--	--	--	--	--	--	--
CaO	--	--	--	--	--	--	--	--
MgO	--	--	--	--	--	--	--	- --
BaO	--	--	--	--	--	--	--	--
PbO (Computed)	0.15	--	--	--	--	--	0.24	1.45
CO₂ (Computed)	0.03	--	--	--	--	--	0.05	0.285
O (Computed)	--	--	--	--	--	--	--	--
Total	99.46	100.06	100.37	100.42	100.01	99.87	99.96	100.15
Sp. Gravity	--	--	7.668	7.536	7.541	7.49	--	7.58
Analyst and year	P. N. Nisenbaum, 1955	Yu. S. Nesterova, 1940	T. L. Pokrovskaya, 1946				V. M. Senderova, 1950	A. A. Petrosyan, 1950*

*Analysis No. 40 is taken from the dissertation of N. M. Prokopenko

of Eastern Transbaikalia, Central Asia and the Caucasus. Some of the material was analyzed by the author (24 analyses), and the rest of the analyses were taken from the collection of the Central Chemical Laboratory of the Institute of Ore Deposits, Petrography, Mineralogy and Geochemistry. The analyses of these specimens (in weight per cent) are given in Tables 1 and 2.

Except for three specimens of fine-grained mixtures of galena with other minerals which were impossible to separate, all analyses were made on carefully picked material. After a microscopic examination the three impure specimens were described as follows:

No. 11 — "a mixture of galena and garnet,"
No. 22 — "galena with an admixture of calcite, barite and negligible amounts of sphalerite,"
No. 27 — "a mixture of galena with barite and anglesite."

The elements occurring in small amounts (less than 0.1%) were determined by the following methods:

Table 2. Description of Galena Samples

Region	Formation	No. of samples	Description of sample
rn Trans-Baikal	Blagodat	1	Medium-grained galena from oxidation zone
''	Smirnov	2	Coarsely crystalline, from massive ore
''	Kadansk	3	Coarsely crystalline, from massive ore
''	''	4	From ore zone
''	''	5	'' '' ''
''	''	6	'' '' ''
''	''	7	'' '' ''
al Asia	Lashkerek	8	From ore vein
''	Arsagan	9	From quartz-barite vein
''	Gavasai	10	Coarsely crystalline, from skarn ore body
''	''	11	Galena with granite, from ore zone
''	''	12	From ore zone
''	Naugarzan	13	From ore vein
''	Gudas	14	From quartz vein
al Asia	Gudas	15	From barite vein
''	''	16	From quartz vein
''	Iokunzh	17	From ore
''	Granitogorsk	18	From fine-grained quartz vein
''	''	19	'' '' ''
''	Cholok-Terek	20	Coarsely crystalline, from quartz vein
''	Kan	21	From ore vein
al Asia	Kan	22	Fine grained
''	Eski-Kan	23	From ore zone
''	Berkutuyasai	24	'' '' ''
''	Karo-o-tek	25	'' '' ''
''	Kok-tyube	26	'' '' ''
''	Kuldzhabashat	27	Mixture of barite and anglesite
hstan	Kzyl-espe	28	From ore body
''	''	29	'' '' ''
''	''	30	'' , '' ''
''	Akchagyl	31	'' '' ''
''	''	32	'' '' ''
''	''	33	'' '' ''
ul Urals	Baevka	34	From ore vein
sus	Sadon	35	Coarsely crystalline
''	''	36	Fine-grained
''	''	37	Coarsely crystalline
''	Upper Zgid	38	From ore
-Caucasus	Upper Kvaisa	39	Medium-grained
''	Kafan (Zangezur)	40	From ore

As — colorimetrically after reduction with sodium hypophosphite

Cu — colorimetrically with potassium ferrocyanide

Cd — polarographically and gravimetrically with Reinecke's salt

Hg — nephelometrically by the method of N. Kh. Aidinyan and A. A. Sukov

Ag — by colorimetric microtitration according to N. V. Maximov's method

Sb — colorimetrically, in the form of iodine-antimony complex with ascorbic acid

Bi — colorimetrically, on the iodine-bismuth complex in the presence of thiourea

Mo — colorimetrically on the ether extract of molybdenum thiocyanate, with $SnCl_2$

Zn — polarographically

Sn — polarographically

Fe — colorimetrically by the sulfosalicylic acid method

Te — colorimetrically with $SnCl_2$ and hydrazine hydrochloride

Amounts from 0.1 to 1% and higher were determined as follows:

Zn — as an anthranilate

Cu — by iodimetry

Te — gravimetrically with $SnCl_2$

Ag — gravimetrically as AgCl

The results of the chemical analyses, expressed in relative atomic amounts, were recalculated to appropriate minerals giving first consideration to the associated ore minerals for a given locality. All macro- and micro-quantities of elements were assigned to minerals usually associated with galena, except for the frequent excess of sulfur which was assigned to native sulfur.

For each sample a composite formula was derived: galena — admixed minerals.

Table 3 presents in abbreviated form the results of recalculation of 40 chemical analyses of galena from the localities listed in Table 2. It gives the frequency of occurrence of the admixed minerals in the analyzed galenas.

The most common admixtures in galena from these localities are argentite, boulangerite, native copper, sphalerite, bismuthinite, and pyrite; less common are cassiterite, pyrrhotite, matildite, arsenopyrite and stannite; wolfsbergite, benjaminite, tetrahedrite and tetradymite are found in a few instances. The most commonly encountered secondary minerals are cerussite, covellite and anglesite. Secondary chalcocite is rare, and willemite and greenockite have been found in only a few specimens.

It may be concluded from this study that:

1) Silver occurs in galena as the simple sulfide, argentite; if silver and bismuth are present together, the former may occur as the silver-bismuth mineral, matildite; and if silver, bismuth and copper are present, as the copper-silver-bismuth mineral, benjaminite.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	quantity of samples
I. Vein minerals and minerals from associated rocks																																									
Quartz	×		×	×	×	×	×	×	×	×	×	×	×	×	×	×			×				×	×	×	×		×	×	×	×	×	×							×	17
Quartz and silicates	×	×	×					×	×	×	×	×	×	×	×	×	×	×		×	×						×								×	×	×				17
Barite	×		×																								×														11
Hematite																								×																	8
Anhydrite											×							×	×		×	×	×				×														2
Dolomite											×																						×								1
Garnet											×	×																													1
II. Associated minerals (inclusions) primary and secondary																																									
Argentite	×	×	×	×	×	×	×	×				×	×		×	×		×	×	×	×	×	×	×	×	×		×	×	×	×				×	×	×	×	×		29
Boulangerite	×	×	×	×	×	×	×	×	×	×	×		×	×			×	×	×		×	×	×	×		×	×		×							×	×		×	×	20
Cerussite	×	×	×						×	×	×	×	×				×			×	×	×	×	×	×	×						×			×	×	×		×	×	19
Native sulfur														×		×											×	×	×		×			×		×	×	×			15
Sphalerite				×	×	×	×	×	×	×		×	×				×	×		×	×	×		×	×	×	×							×	×	×					13
Chalcopyrite								×	×	×					×		×	×			×	×	×											×		×		×		×	11
Bismuthinite																			×								×			×				×		×					10
Pyrite	×					×		×	×					×	×	×			×								×	×		×	×	×	×	×	×	×	×				10
Covellite	×		×			×		×	×					×	×	×											×			×			×	•	•						10
Anglesite											×			×	×	×					×						×								×						8
Cassiterite		×		×																						×													×		5
Pyrrhotite						×							×	×																×											4
Chalcocite													×	×	×		×			×																					4
Matildite																																×	×	×						×	4
Arsenopyrite											×							×															×								3
Stannite	×	×																															×						×		2
Willemite			×																																						2
Wolfsbergite																		×																							1
Benjaminite																																									1
Greenockite																																×									1
Tetrahedrite	×							×				×																													1
Tetradymite																																	×								1

2) Bismuth is captured by galena in the form of the simple sulfide, bismuthinite. More complex bismuth compounds (benjaminite, tetrady-mite, matildite) are seldom found in galena.

3) Arsenic is not common in the analyzed galenas and according to the recalculations occurs only in a few specimens as the arsenic-iron sulfide, arsenopyrite.

4) Antimony is usually present in galena as boulangerite and only in rare cases as other minerals (tetrahedrite, wolfsbergite).

5) The tin content of galenas is due to stannite and cassiterite.

6) The common presence of copper in galena, usually often in con-siderable amounts, is due to an admixture of chalcopyrite, covellite and, less commonly, of chalcocite; less commonly copper occurs as such rare minerals as wolfsbergite and benjaminite. Other minerals contain-ing copper (stannite, tetrahedrite) are not characteristic of galena from our localities.

7) The presence of iron in galena is due to the admixture of chal-copyrite, pyrite and, to a lesser extent, pyrrhotite, arsenopyrite and stannite.

8) Thallium occurs in galena only in spectographic amounts and was not determined chemically.

9) The common presence of vein and country-rock minerals ex-plains the difficulty of obtaining pure material.

10) The common admixture of sphalerite in galena is explained by the constant association of these minerals. In one case, a recalculation of an analysis of galena from the Kadainsk deposit (Eastern Transbai-kalia) revealed the presence of willemite. Inclusions of greenockite in the "relict" galena from the oxidized zone of the Blagodat mine (East-ern Transbaikalia) suggests that the zinc originally present as sphaler-ite inclusions had been removed from galena leaving its isomorphous admixture, CdS.

11) The occurrence of native copper in galena certainly requires further investigation, and may be due either to the presence of the pri-mary mineral (native copper) or to a secondary process in the oxidized zone, especially in those cases in which covellite is also present.

Several samples of galena were subjected to x-ray analysis. All of them gave sharp diffraction patterns. The lattice constants were de-termined by N. I. Organova with the precision of 0.01 Å. Measurements of 13 samples gave values for a_0 ranging from 5.95 to 5.88 Å. Thus, the x-ray examination showed no change in the parameters of the galen-as.

Comparison of data based on microscopic study of polished sections with the results of recalculation of the chemical analyses showed that recalculation to admixed minerals gives a more complete idea of the character and amount of inclusions.

It should be mentioned that the recalculation of chemical analyses to admixed minerals, in some cases, makes it possible to predict what new minerals are likely to be found in a given deposit. For example,

Table 4. Inclusions of Silver, Antimony, Bismuth, and Lead Minerals in Galena, throughout the Metallogenic Provinces, Recalculated from Chemical Analysis Data

Metallogenic province, formation	Mineral inclusions, in molecules per molecule of galena	
Western Trans-Baikal		
odat v nov insk	Argentite Boulangerite Stannite Cassiterite	$2-3 \cdot 10^{-3}$ $1-2 \cdot 10^{-3}$ $1-2 \cdot 10^{-3}$ $1-3 \cdot 10^{-3}$
Central Urals		
ka	Matildite Tetradymite Bismuthinite	$3 \cdot 10^{-2}$ $4 \cdot 10^{-3}$ $4 \cdot 10^{-3}$
Kazakhstan		
Espe agyl	Argentite Matildite Bismuthinite Benjaminite	$2-3 \cdot 10^{-3}$ $3-4 \cdot 10^{-3}$ $2 \cdot 10^{-2} - 1 \cdot 10^{-2}$ $1.5 \cdot 10^{-2}$
Central Asia		
erek gan ai rzan th togorsk k-Terek Kan tuyasai o-tek yube abashat	Argentite Boulangerite Bismuthinite Tetrahedrite Wolfsbergite	$6 \cdot 10^{-4}$ $6 \cdot 10^{-6} - 6 \cdot 10^{-4}$ $4 \cdot 10^{-4}$ $3 \cdot 10^{-3}$ $9 \cdot 10^{-3}$
Caucasus		
Zgid	Argentite Boulangerite Bismuthinite	$1 \cdot 10^{-2}$ $6 \cdot 10^{-5} - 7 \cdot 10^{-3}$ $4 \cdot 10^{-4} - 1 \cdot 10^{-3}$
Trans-Caucasus		
Kveisa (Zangezur)	Boulangerite	$4-9 \cdot 10^{-4}$

ecalculation of the chemical analysis of galena from the Blagodat indicated the presence of stannite, and analysis of a sample of a from the Kadainsk deposit indicated the presence of boulangerite ugh these minerals were not listed in the mineral assemblages

from these localities. Later, boulangerite was found by the mineralo-
gists in the Kadainsk deposit, and the occurrence of tin minerals was
confirmed in all deposits of the Nerchinsk mineralized area.

After the formula for each of the analyzed galenas was derived and a
qualitative estimate of the inclusions of silver, antimony and bismuth
was made, it was possible to compare galena from some of the regions
of the Soviet Union (Table 4). The deposits of different regions from
which galenas were selected for study and (by recalculation of chemical
analyses) were shown to contain silver, antimony and bismuth minerals
in some samples, are listed in Table 4. The table shows also that the
galenas from the southeastern part of Eastern Transbaikalia and galen-
as of Kazakhstan are equally rich in silver, i.e. the amount of argentite
included is the same in both localities. The admixtures of stannite and
cassiterite have been found only in galenas of Eastern Transbaikalia.
The galenas of the middle Urals and of Kazakhstan resemble each other
in their content of inclusions of rare bismuth minerals. The galenas of
Central Asia are poor in argentite and boulangerite, and the rare bis-
muth-silver minerals are absent from them. The characteristic feature
of these galenas is the presence of inclusions of the rare mineral, wolf-
bergite (Granitogorsk) and of tetrahedrite (Lashkerek) which is a rather
common associate of galena in this deposit, according to A. A. Filimon-
ova. The galenas of the Caucasus are similar in their argentite and
boulangerite contents to the galenas of Eastern Transbaikalia, the dif-
ference between them being in the absence of cassiterite and stannite
from the Sadon galena and the absence of bismuthinite from the galena
of Eastern Transbaikalia.

The "native sulfur" revealed by the recalculation of chemical analy-
ses is distributed almost equally among the galenas of these regions.
This is evident from Table 5.

On the basis of this work, i.e. the 24 chemical analyses of galena
from different deposits of the Soviet Union, recalculation of the
analyses (made by the author as well as by other analysts) to the
admixed minerals, and the examination of the x-ray data, the author
concludes that Ag,
Bi, As, Sb, Sn and C
and Fe, do not enter
the crystal lattice of
galena but occur in
independent minerals
which may be pres-
ent as such minute
inclusions that they
can not be detected
by microscopy with
its insufficiently high
magnifications.

Table 5. Distribution of Native Sulfur in Galena,
throughout the Metallogenic Provinces,
Recalculated from Chemical
Analysis Data

Metallogenic province	Sulfur, in molecules per molecule of galena
Western Trans-Baikal	$9 \cdot 10^{-4} - 2 \cdot 10^{-3}$
Central Urals	$7 \cdot 10^{-4}$
Kazakhstan	—
Central Asia	$1 \quad -4 \cdot 10^{-3}$
Caucasus	$5 \cdot 10^{-3}$

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NOTES

PHASE EQUILIBRIA IN THE SYSTEM H_2O-CO_2

N. I. Khitarov and S. D. Malinin

V. I. Vernadskii Institute of Geochemistry and Analytical
Chemistry, Academy of Sciences USSR, Moscow

Abstract

The phase relations in the system H_2O-CO_2 up to a temperature of 330° and pressure of 600 kg/cm² have been studied. The presence of critical transitions of the system has been established. The pressure of CO_2 lowers the critical temperatures. On the basis of the diagram, H_2O-CO_2 considerations concerning the behavior of hydrothermal waters under deep-seated conditions are stated.

Investigation of endogenic processes requires a detailed knowledge of the phase relations in the system water—carbon dioxide which is so frequently encountered in nature. Carbon dioxide plays an essential role not only in hydrothermal processes but also in many metamorphic processes which involve greater or lesser amounts of water.

The data available in the literature on the solubility of carbon dioxide in water under pressure, which are of great interest to geochemists, cover the range from 0 to 25°C and in two cases only, extend to 100°C and 120°C [1,2]. The interesting region of higher temperatures so important for the understanding of hydrothermal processes still remains unexplored.

For this reason a series of experiments were made in the Laboratory of Magmatic Processes on phase equilibria in the system H_2O-CO_2 at temperatures from 200°C to 300°C and under pressures up to 600 kg/cm². This note presents the general diagram of the system. A more detailed account of the investigation will be published later in a special paper.

The coordinates of the general diagram are composition (in molecular per cent) and pressure (kg/cm²). The curves on the right represent the composition of the liquid phases, those on the left, the composition of the gaseous phases in equilibrium with them. A number of conclusions can be drawn from the diagram.

1. The solubility of carbon dioxide in water increases noticeably with increase in pressure and temperature, reaching, for example, the value of 200 g/l CO_2 at P = 400 kg/cm² and T = 300°C.

2. At a certain temperature depending on pressure the isobaric solubility curve for carbon dioxide in water passes through a minimum

n be seen in the lower part of the diagram. This is not unexpect-
or this phenomenon is known in thermodynamics for phase equi-
in solutions at high temperatures and pressures as, for example,
the system SO_2-N_2 [3].

As shown by the analysis of the gas phases in equilibrium at
ent pressures for the 300° isotherm, the content of CO_2 in the
passes through a maximum because of the increased tendency of a
ressed gas to dissolve liquid as the pressure rises.

The convergence of the composition curves of the liquid and
ous phases may result in formation of loops enclosing regions of
stence of the two phases. Beyond these loops, as the pressure
ases, the system becomes homogeneous, and this is accompanied
itical phenomena. For the 200° and 250° isotherms, the curves
fail to form loops with increasing pressure, and the curves will
through maxima and minima.

he two branches of an isotherm originate at the same point, which
responds to the pressure of saturated vapor of pure water. As the
erature rises, the loops of the isotherms are drawn closer to the
ate and in the limit approach a point representing the critical
sure of pure water (225.5 kg/cm²). In an earlier study of the
m carbon dioxide-water [4] indirect indications were obtained of
owering of critical temperature of the solution with increase in
n dioxide content. This interesting characteristic of gas-liquid
ms, that the critical temperatures lie below the critical tempera-
of the solvent, is clearly indicated by the new data on the diagram.
issolved gas lowers the critical temperature of the solvent. This
opposite of what is known of salt-water systems, in which an ad-
of salt usually raises the critical temperature.

hese experimental data broaden our knowledge of the phase rela-
in the CO_2-bearing thermal waters at a considerable depth. It
ws from these data that the amount of carbon dioxide dissolved in
at high temperatures must be considerable and that under certain
tions CO_2 and H_2O must be completely miscible. These conditions
beyond the temperatures of 200-300°C and the pressures of 400-
g/cm². These pressures correspond to depths of 4 to 5 km.

the mixture of water and carbon dioxide behaves like a mobile
ous mixture which not only aids the transfer of heat but also the
ation of active solutions in the areas of condensation far removed
the place of separation of the mixture.

epending on the geological setting, these solutions may cause the
rance of typical hydrothermal products or of metamorphosed
s of considerable areal extent.

dging from the water-carbon dioxide phase diagram, the sharpest
tions in the effect of carbon dioxide, both dissolved and free, on
idespread carbonate rocks must occur at temperatures exceeding
and up to the critical temperatures. In this range, within a nar-
imit of pressure changes, there must occur a very frequent alter-
between solution and precipitation of solid (mineral) carbonate
s.

Percentage of molecular CO_2
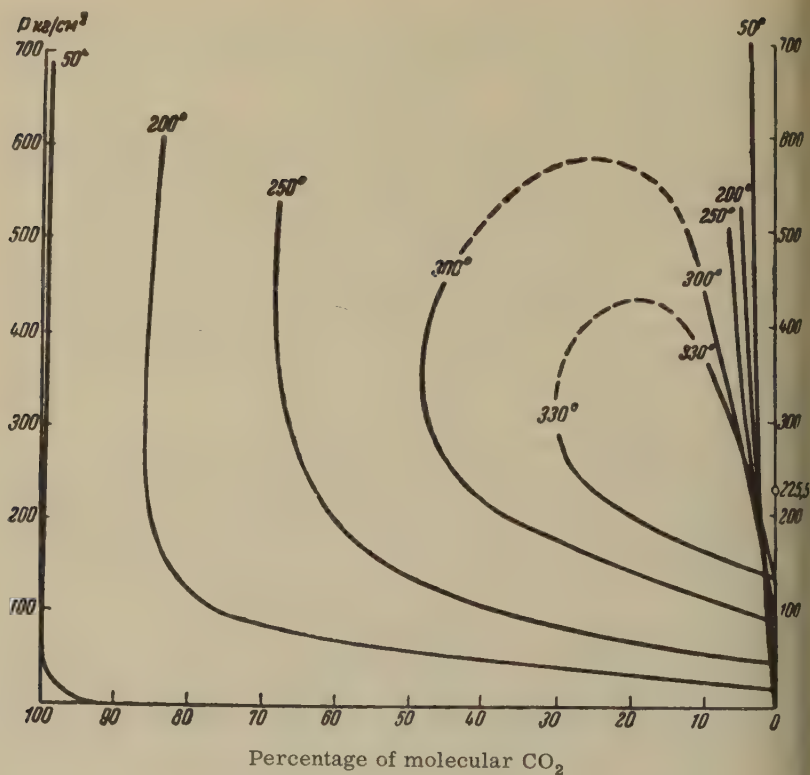
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BORON PROFILES BY THE NEUTRON METHOD

V. I. Baranov and V. K. Khristianov

V. I. Vernadskii Institute of Geochemistry and Analytical
Chemistry, Academy of Sciences USSR, Moscow

Abstract

1 x 10^7 n/sec neutron source is placed under a water reflector at a dis-
of 24 cm from a direct neutron detector. The detector, together with the
ring instrument, slides on the surface at the rate of 4–5 kilometers per
creating a sliding soil-water contact. This increase of the boron oxide
ntration in the soil by 0.01% corresponds to the decrease of the neutron
ensity by 5% relative. The method can be used for studying the distri-
of boron in soil for the purpose of speedily defining perspective areas
prospecting for new borate deposits.

1953, Academician A. P. Vinogradov proposed a method of neutron
ng with the use of an absorbing element, such as boron [1,2], and
uggestion was successfully tested by his associates. Further in-
gations showed that the method of neutron capture is not limited to
ng of boreholes but has a much wider field of application. For ex-
, the method of determination of boron concentrations in rock
les by neutron absorption is now in its second year of development

l winter of 1957, S. S. Korobov, Chief Geologist of the Inder Geo-
l Expedition, in a private conversation, expressed his ideas on
enrichment in soils overlying ore bodies and suggested the pos-
ty of rapid determination of boron concentration in soils by the
on method. We constructed a suitable apparatus and tested it in
eld.

like the neutron logging of boreholes where measurements are
in an isolated medium of infinite extent, the analysis of distribu-
f boron in soils is complicated by the fact that measurements must
de at the soil-air interface. This boundary causes strong impov-
ment of the soil in neutrons and makes it impossible to make
le determinations of their density.

decrease the detrimental effect of the soil-air boundary and re-
ce the conditions of an infinite isolated medium, we used a water
ctor sliding over the soil with the measuring instrument and creat-
sliding contact between soil and water. A neutron source with the
sity of $1 \cdot 10^7$ n/sec was placed under the water reflector at a dis-
of 24 cm from the oriented end of the neutron detector.

e reflector was pulled by an automobile with the velocity of 4–5
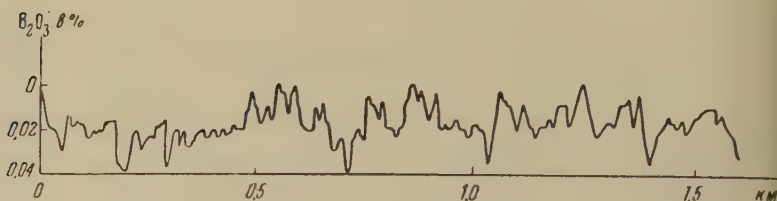
Variations in Concentration of B_2O_3 Along the Profile

km/hr and readings were taken from a dial and pointer arrangement. The sensitivity of the method, 0.01% B_2O_3 to 5% minimum, was determined in an artificially prepared experimental field. The method is sensitive to the depth of 10-15 cm. An example of the record registering variation in the concentration of boron oxide in soil to within 0.04% over a distance of 1.5 km is shown above.

The high sensitivity of the method makes it worthwhile to try it in rapid exploration for borate deposits in salt dome structures, mainly of the piercement type, where the evaporites crop out on the surface. At present, as in the past, borometric surveys are done by sampling on a grid with subsequent spectrographic examination of the samples.

The great advantage of the new method, as compared with the usual methods of metallometric surveys, is the continuity of readings obtained by it along a profile and the efficiency of analysis which makes sampling unnecessary. A serious shortcoming of the new method is that it can be used only in the regions of low relief.

Research on the development of the method continues.

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NEW DATA ON THE DISTRIBUTION OF INDIUM IN MINERALS OF THE OXIDIZED ZONE

A. S. Vishnevsky

T. G. Shevchenko State University, Kiev

Abstract

w data on the chemistry of indium in the oxidized zone of the tin-lead-zinc
t of Sarybulak (Central Tian-Shan) have been obtained. The results of the
al analysis of 32 samples of minerals and their mixtures enable us to
he following conclusions: High indium concentrations are observed in the
on zone. Hypogene ores composed of sulfides of Sn, Cu, Zn, Pb, Sb, Fe,
ssiterite were the source of indium. Ferric hydroxides, hydrocassiterite
dheimite are the mineral concentrators of indium in the supergene zone.
ncentration of indium probably may be explained by the high absorptive
ties of the gels of Fe, Sn hydroxides and of the complex gel of bind-
e composition, in conjunction with the easy polarizivity of the indium
unds.

ubstantial number of papers have been dedicated to the subject of
dium content of rocks, ores, and minerals. However, data on the
emistry of indium are principally related to its endogenetic for-
; information on the behavior of this exceedingly rare and dis-
ated element in the supergene zone is sparse and requires more
and accuracy.

e publication "Geochemistry of Indium" [1] allots very little
to the geochemical history of indium during the supergene stage.
t has been said could be reduced to the following statement:
ased concentrations of indium do not take place in the oxidation
f sulfide deposits. On the contrary, as a rule the process of
r dissemination of indium takes place. Increased concentrations,
do occur, are of a local nature. One may think that the presence
um in some minerals in the oxidation zone could be explained by
rbtion phenomenon (ochre, kaolinization products, scorodite, and
." A second publication [2] indicates the following: "In the ma-
on Central Asia no reference was found to increased concentra-
indium in the oxidation zones of sulfide deposits." The litera-
hows either absence of indium or its presence in very minute
ties in most minerals of the oxidation zone. For example, indium
ent in limonite from the following deposits of the U.S.S.R.:
h-Burun, Kahlilovo, Almalyk, and others [1]. Fifteen samples
onite from various areas in Finland and goethite from Pitkyaranty
elsewhere show no indium. Traces and increased concentra-
f indium have been established in the yellow ochre in the Aurora
-Chegyl deposits in Kazakhastan [1].

New data on the geochemistry of indium in the oxidation zone, which we believe to be of interest, were obtained as a result of the investigation of the tin-polymetallic deposit at Sarybulak (central Tien-Shan, Ak-Zoo Mountains).

We shall present a short geologic description of Sarybulak before presenting the results. The deposit consists of a number of metasomatic ore bodies which are located in the exocontact of a small massif of biotite porphyry and hornblende-biotite granite. The granite penetrates thick, gray Middle Paleozoic limestone (D_3^2 -C_1^2), which changes into medium-grain white marble in the contact zone. Skarn bodies consisting of garnet of the andradite-grossularite series, hedenbergite, quartz, calcite, scapolite, and other sparsely distributed minerals were observed along the contact.

The ore body which has been studied in greatest detail is situated in marble, about 120 meters from the contact with granite. It is about 12 meters thick on the average and 70 meters long. To a depth of 25 meters the ore body consists exclusively of oxidized ores, among which there are found very rare and isolated fragments containing the following primary minerals: quartz, calcite, and cassiterite. The following were established among the supergene minerals (given in order of prevalence): *principal*—oxides and hydrous oxides of iron and manganese (goethite, hydrous goethite, hydrous hematite, pyrolusite, psilomelane, hausmanite, manganite), ice and calcite; *less common*—bindheimite, calamine, malachite, cassiterite and hydrous cassiterite, and quartz; *rare*—cerussite, mimetite, pyromorphite, chalcedony, cuprite, tenorite, native copper, vanadinite, and duftite.

At first indium was found in the deposit spectroscopically, in samples of hydrous iron oxides and secondary tin minerals. Thirty-two different minerals and their mixtures were analyzed chemically in order to determine their indium contents and to obtain a more accurate picture of indium distribution in the oxidation zone of the Sarybulak deposit. (Analyst: N. V. Obolonchik, Institute of General and Inorganic Chemistry, Academy of Sciences, Ukranian S.S.R.) Eleven of these samples were subjected to a complete analysis and three were analyzed only partially (analysts: T. N. Nazarchuk and N. V. Obolonchik from the same institute).

The result of the analyses are given in Tables 1 and 2.

On the basis of the results it is possible to arrive at the following conclusions:

1. The source of indium in the oxidation zone of the Sarybulak deposit is supergene ores consisting of Sn, Cu, Zn, Pb, Sb, Fe sulfides and cassiterite.

2. The formation of high indium concentrations in the oxidation zone is conditioned by the geology of the deposit and the mineralogic composition of the ores. The surrounding carbonate medium and the great number of calcite veins in the ore body led to the rapid conversion of acid solutions to alkali in which there is no migration of indium.

3. The minerals which act as concentrating agents for indium in

Table 1. Indium Content of Minerals in the Oxidation Zone

Sample index	Composition % by weight	Short description of sample
9/6	0.210	Powder-like, greenish-yellow, light hydrous cassiterite
7/18	0.145	Yellow-brown, hydrous cassiterite with inclusions of Fe_2O_3
5/2	0.045	Friable light-yellow hydrous cassiterite
7/11	0.091	White-yellow, hydrous cassiterite, thinly dispersed
9/2	0.089	Bright yellow earthy bindheimite
C-19	0.186	Tightly concreted aggregate of colloform malachite and bindheimite
C-27	Not found	Brownish yellow bindheimite, weakly cemented
P-17	0.120	Powdery mixture of bindheimite and limonite
C-21/1	0.410	Cherry-red, powdery hydrous hematite
P-7	0.230	Hydrous hematite in voids in brecciated quartz
P-8	0.590	Hydrous hematite, associated with bindheimite
P-11	0.190	Red hydrous hematite in limonite
P-15	0.190	Hydrous hematite mixed with clay minerals
P-6	0.350	Friable hydrous goethite of brown color
3/8	0.026	Dense hydrous goethite, colloform, layered texture
P-13	Not found	Colloform limonite, thick layering
P-18	0.073	Earthy limonite
P-19	0.098	Friable hydrous goethite
C-10	0.043	Goethite of a coarse box-like texture
7/10	0.430	Hydrous goethite with a relict lamellar texture
3/14	0.016	Colloform hydrous goethite, layered texture
3/16	0.055	Reddish-brown goethite, powdery
7/8	0.100	Powdery mixture of limonite and bindheimite
P-9	0.210	Dense aggregate of hydrous iron and manganese oxides
P-10	0.040	Dense psilomelane
3/4	0.020	Earthy psilomelane, in places dense
C-6	Not found	Cryptocrystalline pyrolusite
5/1	Not found	Colloform pyrolusite
C-34	Not found	Calamine, large water-transparent crystals
212	Not found	Clay minerals (illitic hydromicas)
232/1	0.170	Supergene cassiterite with light colored sections
232/2	0.240	Supergene cassiterite with dark colored sections

:ks:

um was determined by the polarographic method.

results of analyses 9 and 11 were checked by the gravimetric method.

mineralogic composition of the samples was determined on the basis of

al, thermal and X-ray investigations.

oles C-27, P-18, and P-19, were taken from the outcrop of the ore body.

rest of the samples were taken from depths of five to twenty-five meters.

Table 2. Chemical Composition of Minerals in the Oxidation Zone

Oxides	Sample index													
	5/2	7/11	C-27	C-21	C-10	7-10	3/14	3/16	7/8	C-6	5/1	C-34	232/1	232/2
SiO_2	4.44	3.05	2.31	2.07	1.42	0.97	1.40	2.50	4.32	1.29	7.43	24.78	1.27	1.51
TiO_2	--	--	--	--	--	--	--	--	--	--	--	--	0.46	0.40
SnO_2	55.42	69.47	2.45	0.14	0.21	0.63	0.12	0.11	2.58	3.91	--	--	97.90	98.31
Fe_2O_3	10.50	7.68	2.21	69.44	77.0	74.56	79.00	74.57	31.79	18.82	17.91	--	0.66	0.39
Al_2O_3	--	--	1.76	4.56	8.50	9.34	5.00	9.49	10.81	--	--	--	--	--
FeO	--	--	--	0.33	0.34	0.22	0.13	0.15	0.73	Traces	--	--	--	--
CaO	0.79	--	2.66	--	none	none	none	none	none	--	--	--	--	--
MnO	--	Traces	--	0.07	0.14	0.10	1.15	2.84	0.80	--	--	--	Traces	Traces
MgO	--	--	--	0.27	0.39	0.21	0.43	0.23	0.31	--	--	--	--	--
PbO	7.07	none	38.82	4.72	0.0032	0.39	0.022	0.019	12.16	0.17	0.04	--	--	--
ZnO	--	--	0.19	none	none	none	none	none	none	6.93	1.83	65.80	none	none
CuO	--	0.11	0.21	0.30	0.34	1.38	0.23	0.21	1.32	0.002	0.21	--	--	--
MnO_2	--	--	--	--	--	--	--	--	--	59.40	67.48	--	--	--
Sb_2O_5	15.37	12.28	40.42	10.66	--	0.74	--	--	22.40	--	--	--	--	--
As_2O_5	2.57	--	4.34	--	--	--	--	--	--	--	--	--	--	--
P_2O_5	--	--	--	0.53	0.94	0.30	0.30	0.20	0.68	none	none	--	--	--
SO_3	--	--	0.37	1.15	1.70	1.71	1.20	0.85	0.38	0.12	0.04	--	--	--
Ign. loss	3.28	7.88	4.89	5.89	9.26	10.44	11.13	9.01	7.27	10.66	9.93	8.54	--	--
Total	99.44	100.44	100.63	100.13	99.76	100.77	99.98	100.48	96.55	100.01	--	99.12	100.29	100.61

supergene zone are the hydrous oxides of iron (hydrous hematite, ...ite, hydrous goethite), hydrous cassiterite and bindheimite; all ...e are thinly dispersed metacolloidal substances. The presence of ...m in psilomelane is apparently explained by the presence of ...nite in it.

The phenomenon of indium concentration should most likely be ...ained by the high absorbtion properties of Fe and Sn hydrous oxide ...and the complex gel of bindheimite composition in conjunction ...the ease of polarization of indium compounds.

Concentration of indium by positively charged colloids of hydrous ...oxides and the absence of indium in negatively charged colloids ...ganese dioxide, clayey minerals) make it possible to assume that ...m is not present in the oxidation zone in the form of cations; ap-...ntly it forms hydrous oxide compounds or perhaps it is absorbed in ...orm of individual atoms.

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REMOVAL OF WATER-SOLUBLE SUBSTANCES FROM THE PYROCLASTIC ROCKS OF THE VOLCANO BEZYMYANNYI

I. I. Tovarova

Volcanological Laboratory, Academy of Sciences USSR, Moscow

Abstract

The 1955-1956 eruptions of the Bezymyannyi Volcano of the Kamchatka Penninsula resulted in expulsion of 0.9×10^9 tons or a cubic kilometer of ash; the weight of the agglomerate ejected was estimated at 3.3×10^9 tons. On the basis of analytical data, the eruption brought to the surface about 20 million tons of easily soluble material. Water samples (of pH6) collected from hot springs of 65°C are highly mineralized being enriched in sulfate and chlorine ions, CO_2, and Ca. Comparison of artificial leaches of the Kamchatka Volcano agglomerate prepared at room temperature show less mineralization than natural surface material, probably because of lower temperature and smaller volume of leach matrix present in the artificial system.

The 1955-1956 eruption of the volcano Bezymyannyi in Kamchatka was one of the greatest eruptions of the past fifty years. It may be classed with such grandiose eruptions as those of Krakatou (1883), Katmai (1912), Mont Pelee (1902), etc. An enormous amount of pyroclastic material was ejected during the eruption of Bezymyannyi.

During the first months the volcanic activity was characterized by numerous explosions of the Vulcanian type accompanied by ash showers within a radius of over 100 km. During the initial stages of the eruption between October 22, 1955, and March 30, 1956, a 25 mm layer of ash was deposited at the settlement of Klyuchi (45 km from the volcano). This layer is equivalent to 15 kg of ash per square meter. The total amount of ash erupted during this period exclusive of the March 30, 1956 eruption, is estimated at about 0.5 km³. The culmination of the eruption, a great explosion, occurred on March 30, 1956. A fan-shaped jet of incandescent ash was obliquely ejected from the top of the volcano in a southeasterly direction. Unusually thick pyroclastic flows forming an agglomerate deposit many meters in thickness over an area of 50 km² emanated from the resulting explosion crater. The volume of the ejected unconsolidated agglomeratic material is about 1.8 km³. An immense dark cloud of ash over the crater and the pyroclastic flows rose to a height of about 40 km. To the northeast of the volcano a strong ash fall traversed a distance of more than 400 km. During three and a half hours a 20 mm layer or 24.5 kg/m² of ash was deposited at

chi. The volume of ash that fell during the main explosion is esti-
ed at 0.5 km^3.

he incandescent ash of the directed explosion covered an area of
t 500 km^2. The vast amount of incandescent material caused sud-
melting of snow. The melt waters mixed with ash and rocks to
mudflows which flowed for about 90 km, destroying trees and
h in their course. These mudflows entered the Kamchatka River.
additional volume of water in the river amounted to approximately
illion cubic meters. The sudden change in hydrochemical condi-
resulted in mass destruction of fish in the river.

the spring and summer of 1956, numerous streams flowing through
agglomerate cut deep ravines in the unconsolidated material. In
places water flowed on the surface of the unconsolidated agglom-
and gradually percolated into it, emerging at the contact between
agglomerate and a moraine as hot springs. The newly formed
ks and rivulets undermined the walls of their "canyons" and hot
merate fell into the water. This caused steam explosions—pecu-
eruptions which threw ash as high as 200 - 300 m into the air.
stream waters were sometimes so saturated with the unconsoli-
pyroclastic material that the water became muddy, but very
le. Large rocks were transported by these flows.

s the result of rains and rapid melting of snow (which is 2 to 3 m
in Kamchatka) large masses of water continuously percolated
gh the agglomerate and ash deposits and carried soluble materials
the Kamchatka River and ultimately into the Pacific Ocean.

the summer of 1956 two samples of water were taken from the
merate deposit. Sample 785 was taken from a hot spring at a
ct between the agglomerate deposit and underlying moraine. The
g is fed by surface waters seeping through the agglomerate.
ng their passage through the hot agglomerate these waters leached
oluble substances from it. The temperature of the spring at the
of sampling was 65°C. The spring was temporary and disappeared
rd the beginning of autumn. Sample 787 was taken from a surface
m flowing in a small valley cut in the agglomerate. Its tempera-
was not over 20°C.

nalyses of the samples are given in Table 1. Both water samples
highly mineralized (4-5 g/l) and have a high content of sulfate and
ine ions, carbon dioxide, calcium and other elements. However,
samples have an almost neutral pH.

order to determine the amount of mineral matter that can be
ported by surface waters into the ocean, the easily soluble sub-
es were extracted from the pyroclastic rocks. The extraction was
from unconsolidated material with a grain size of less than 1 mm.
ous extracts obtained by leaching 100 g samples four times with
amounts of water at room temperature for 48 hours were
zed.

is method of extraction reproduces in miniature the leaching
ss of unconsolidated pyroclastics by surface waters. An

Table 1. Chemical Analysis of Water Traversing Agglomerates
of the Volcano Bezymyannyi

	785		787	
	mg/l	mg-equiv	mg/l	mg-equiv.
NH_4^+	178	9.88	50.46	2.80
$Na^+ + K^+$	1025	43.55	403.00	17.52
Mg^{2+}	269	22.11	375	30.82
Ca^{2+}	428	21.35	686	34.23
Fe^{3+}	9.7	0.52	2.88	0.15
Al^{3+}	11.87	1.32	0.46	0.05
Total	1921.57	98.73	1517.8	85.57
Cl^-	782	21.95	782	21.95
SO_4^{2-}	1070	22.27	1470	30.60
HCO_3-	3446	56.51	2013	33.01
Total	5298	98.73	4265	85.56
H_2SiO_3	169		73	
General mineralization	5496		4775	
CO_2, general	1265		1111	
Dry residue	5850		4905	
pH	6.6		6.7	

Table 2. Chemical Analysis of Water Extracts from Volcanic Ash
and Friable Material of Agglomerates

	I		II		III	
	mg/100g	mg-equiv.	mg/100g	mg-equiv.	mg/100g	mg-equiv.
NH_4^+	10.80	0.49	7.20	0.33	10.80	0.49
Na^+	8.10	0.35	5.15	0.23	6.63	0.29
K^+	3.11	0.08	1.68	0.04	1.70	0.04
Mg^{2+}	21.50	1.77	10.20	0.84	3.11	0.26
Ca^{2+}	157.00	7.83	81.20	4.05	54.00	2.69
Fe^{2+}	2.22	0.08	2.22	0.08	1.56	0.06
Fe^{3+}	3.00	0.16	2.18	0.12	1.18	0.06
Al^{3+}	3.02	0.34	2.93	0.33	1.98	0.22
Total	208.75	11.10	112.76	6.02	80.96	4.11
$Cl-$	95.88	2.70	55.04	1.55	22.70	0.64
SO_4^{2-}	400.40	8.33	198.40	4.12	165.00	3.41
HCO_3-	29.30	0.48	24.40	0.40	20.49	0.33
Total	525.58	11.51	277.84	6.07	208.19	4.38
H_2S	0		0		0	
H_2SiO_3	4.99		4.59		3.58	
General mineralization	724.67		390.60		278.90	
CO_2, general	176.0		211.20		240.50	
Dry residue	807.7		411.80		254.13	
pH	5.80		5.00		5.30	

ximation of the amount of material carried out by leach water is
by this method of extraction.

e pH value of the combined aqueous extracts (400 ml) was deter-
d and the extracts were analyzed for NH_3, Cl^-, CO_2, HCO_3, SiO_2,
nd dry residue. The residue was analyzed for R_2O_3, Ca^{2+}, Mg^{2+},
, Na^+ and K^+. Results are shown in Table 3 where: I. is
us extract from the ash deposited in the vicinity of the volcano
g the initial phases of eruption; II. is aqueous extract from the
the main explosion and III. is aqueous extract from the agglom-

can be seen from Table 2, the aqueous extracts obtained in the
tory are less mineralized than the natural surface waters.
ently, under natural conditions leaching is more intensive. In
of this, "incomplete" extractions were made in the belief that
rovide a more objective estimate of the amount of substances
d out under natural conditions. Even so, the estimated amount
erial carried out to the ocean is considerable.

sidering the volume of the pyroclastic material cited above and
the specific gravity of the unconsolidated material as 1.8, the
of the ejecta was estimated as follows: the weight of ash of the
nd main eruptive phases amounts to $0.9 \cdot 10^9$ tons. The weight of
glomerate is $3.3 \cdot 10^9$ tons. Assuming that the fine fraction of the
erate constitutes about 80% of the total mass, we obtain the
t of easily soluble material in the pyroclastic ejecta shown in
3.

Table 3. Total Amount of Water-soluble Matter (in tons)
in Pyroclastics of Bezymyannyi Volcano

	I	II	III	Total
NH_4^+	$9.7 \cdot 10^4$	$6.5 \cdot 10^4$	$28.6 \cdot 10^4$	$44.8 \cdot 10^4$
Na^+	$7.3 \cdot 10^4$	$4.6 \cdot 10^4$	$17.3 \cdot 10^4$	$29.2 \cdot 10^4$
K^+	$2.8 \cdot 10^4$	$1.5 \cdot 10^4$	$4.5 \cdot 10^4$	$8.8 \cdot 10^4$
Mg^{2+}	$1.9 \cdot 10^5$	$0.9 \cdot 10^5$	$0.8 \cdot 10^5$	$3.6 \cdot 10^5$
Ca^{2+}	$1.4 \cdot 10^6$	$0.7 \cdot 10^6$	$1.4 \cdot 10^6$	$3.5 \cdot 10^6$
$Fe^{2+}+Fe^{3+}$	$4.6 \cdot 10^4$	$4.0 \cdot 10^4$	$7.3 \cdot 10^4$	$15.9 \cdot 10^4$
Al^{3+}	$2.7 \cdot 10^4$	$2.6 \cdot 10^4$	$5.2 \cdot 10^4$	$10.5 \cdot 10^4$
Cl^-	$8.6 \cdot 10^5$	$5.0 \cdot 10^5$	$6.0 \cdot 10^5$	$19.6 \cdot 10^5$
SO_4^{2-}	$3.6 \cdot 10^6$	$1.8 \cdot 10^6$	$4.4 \cdot 10^6$	$9.8 \cdot 10^6$
HCO_3^-	$2.6 \cdot 10^5$	$2.2 \cdot 10^5$	$5.4 \cdot 10^5$	$10.2 \cdot 10^5$
H_2SiO_3	$4.5 \cdot 10^4$	$4.2 \cdot 10^4$	$9.5 \cdot 10^4$	$18.2 \cdot 10^4$
Total	$6.6 \cdot 10^6$	$3.5 \cdot 10^6$	$7.7 \cdot 10^6$	$17.8 \cdot 10^6$

rding to a very modest estimate, the eruption of Bezymyannyi
asin of the Kamchatka River brought to the surface about 20
tons of easily soluble substances. These data suggest the scale

of the geochemical processes on the earth's surface for which large
volcanic eruptions ejecting great volumes of pyroclastic material are
responsible.

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CHRONICLE

Tenth General Assembly of the International Astronomical Union

(Moscow, August 1958)

1. SYMPOSIUM ON THE EVOLUTION OF METEORITIC MATTER

symposium on the problems of meteoritics was held in Moscow on
st 18, 1958, as a part of the program of the Xth General Assembly
International Astronomical Union (Moscow, August 12-20, 1958).
articipants were students of meteoritics, geochemists and as-
ners of the Soviet Union and a number of delegates to the IAU
ess from England, East Germany, Canada, USA, France and
n.

e meeting was devoted to the discussion of different questions of
mistry of meteorites and their formation from asteroids in con-
n with the general problem of the origin of meteorites. Seven
s were presented at the meeting, of which three were read (papers
P. Vinogradov, V. G. Fesenkov and H. Brown) and the rest were
uted in the form of abstracts.

is paper, "Meteorites and the earth's crust," Vinogradov showed
basis of experimental data that the content of trace elements in
ites is five to ten times as high as in dunites. He presented the
esis that dunites represent the residual material of the earth's
remaining after the more fusible fraction, the parent material
igneous rocks, had been melted out of the mantle.

al melting of chondritic material established the character of
ocess and suggested possible relationship between chondrites
hondrites. The differentiation of terrestrial material, however,
a different course because of the presence in the upper parts of
th of volatile and other mineralizers.

isotopic composition of C, H, O, S and the inert gases in differ-
teorites shows that the isotopic ratios in meteorites and in ter-
l rocks are different. This again indicates that the processes of
ntiation and their temperatures are different in meteorites and
ks of the earth's crust.

he basis of experimental data, Vinogradov arrives at the conclu-
at the processes of differentiation in different types of meteorites
ferent from those in the earth's mantle and crust. He believes,
icular, that the ironstone meteorites form as the result of aggre-
of iron and silicate melts.

. Fesenko reported on the "Conditions of disintegration of

asteroids according to the data of photometric investigations of zodiacal light," in which he pointed out that zodiacal light is caused by the dispersion of sunlight by minute dust particles which are always replenished by the continuous breakdown of asteroids and meteorites.

The author compared the lines of equal illumination due to zodiacal light (based on the data of the 1957 expedition to Egypt) with theoretical lines of equal illumination computed from the distribution of asteroids according to the angles of inclination of their orbits to the ecliptic. From these data the velocity of dust particles released by the disruption of an asteroid was computed as 7 - 10 km/sec. This value is somewhat higher than expected if it is assumed that collision between asteroids moving in their orbits in the same direction is the cause of their disintegration.

H. Brown (USA) in his paper on the "Distribution of Cr, Mn, Ti, Fe, Co and Ni in meteorites," reported the results of determination of these elements in chondrites by fluorescence.

He found that in what he calls the chondrites of the "principal sequence," the following ratios are constant: $Ni/Co = 15.8 \pm 0.1$, $Cr/Mn = 1.03 \pm 0.01$ and $Mn/Ti = 4.07 \pm 0.02$. The determination of the ratios of iron, cobalt and nickel to chromium and manganese established the existence of four groups of chondrites (besides the carbonaceous), each of which is characterized by constancy of these ratios. It has been found that the absolute content of Co and Ni is higher in finds than in observed falls, but the reason for this is not clear.

F. Whipple (USA) read a paper on the "New results of study of meteorites and micrometeorites" in which he presented data on the fission products in iron meteorites produced by the action of cosmic rays. Measurement of the content of H^3, He^3, A^{39} and A^{38}, give new age determinations for meteorites and the first measurements of the sizes and masses of two large meteorites, Carbo and Grant, before their entry into the atmosphere.

An investigation of micrometeorites collected at an altitude of more than 15,000 meters indicates the existence of meteorites with the size of the order of 10μ and low density and of much smaller magnetic particles (identified by the electron microscope) with high density.

H. Urey (USA) read a paper on the "Metallic constituents of chondrites" in which he gave the results of a metallographic study of iron-nickel inclusions in eleven chondrites and one achondrite. Among the inclusions are kamacite particles in the form of large crystals with Neumann lines and inclusions with polycrystalline structure. Taenite particles of different shapes and sometimes with inclusions of plessite were also found. Both kamacite and taenite particles show signs of deformation and occur as isolated inclusions or in contact with each other.

From these observations the author draws the conclusion that the metallic particles are minute fragments of large masses and in many cases could not have formed in the bodies in which they are now found. It is believed that the silicate minerals as well as kamacite and taenite

formed as the result of slow cooling of large masses which were
broken up into very small fragments and that still later the frag-
were accumulated in other (secondary) bodies.

e meteorites could have acquired the individual details of struc-
not only in the primary bodies but also during the process of dis-
ation and in the secondary bodies. Some chondrites are glassy
contain undifferentiated metal indicating that they were melted and
d without crystallization.

me metallic particles show signs of a second heating in the form
bayed edges on taenite, polycrystalline kamacite, inclusions of
e in kamacite, etc. It is believed that this occurred during dis-
on of the primary bodies and that temperatures of about 500°C
reached. The presence of glassy chondrules indicates that locally
r temperatures were attained.

A. Yavnel presented a paper on "Certain regularities in the com-
on of meteorites" in which he showed that on the basis of the
between the metallic and silicate phases all meteorites may be
ed, in the first approximation, into six subclasses: achondrites
n Ca, achondrites poor in Ca, chondrites, mesosiferites, pallasites
siderites, and on the basis of the composition of the phases (the Ni
nt in the metal and the FeO content in the silicates), into five
s. This subdivision is the basis of the author's classification of
orites according to chemical and mineralogical composition and
ture.

mparison of different groups of meteorites in a given subclass
ls a relationship between the composition and the ratio of the
s known as Prior's "group" regularity. It is supposed that the
orites of each group with similar composition of phases (similar
nt of essential elements) are genetically related and were derived
the same asteroid, possibly with a layered structure.

om the data on the number of chondrites and siderites of different
osition a relationship has been discovered between the composition
mounts of the metallic and silicate phases in different asteroids
is known as "Prior's primary regularity." It is supposed that
egularity is due to the differentiation of matter occurring before
rmation of individual asteroids.

study of iron meteorites leads to the supposition that their struc-
were formed at temperatures below 450°C and at different pres-
(below 10^5 atm.).

e regular variation in the structure and composition of meteorites
sts that the changes in meteorite structures, including metamor-
on, occurred before the disruption of asteroids as the result of the
ex thermal history of these bodies and not as the result, for ex-
, of their approach to the Sun.

G. Kvash, in his paper "On achondrites," discussed the petro-
ic and petrochemical characteristics of individual types of achon-
. The amphoterites, which belong to the feldspar-free group of
drites, are actually crystalline chondrite breccias with a small

admixture of nickel-rich iron. This confirms the opinion that they be-
long to the chondrite and not to the achondrite subclass. A number of
details of structure and mineralogy of other types of achondrites,
chassignites, nakhlites and chladniites and also of carbonaceous chon-
drites were mentioned.

In comparing the chemical composition of achondrites, Zavaritskii's
method of petrochemical study of igneous rocks was used. An addition-
al vector (on the SBC plane) was introduced into the vector diagram of
compositions to show the ratio of nickel to nickeliferous iron.

The diagram shows the distribution of achondrites according to
groups and types within the groups and the nature of variation in chemi-
cal composition correlated with the mineralogical composition. It
shows also the close similarity of the chemical composition vectors
and their distribution in achondrites and in different types of terrestrial
rocks. The diagram makes it clear that the variety and the character
of variation among the achondrites are the same as in the ultrabasic
and basic rocks formed in the earth's crust.

The presentation of papers was followed by a discussion.

A. A. Yavnel

2. SYMPOSIUM ON THE ORIGIN OF THE EARTH AND PLANETS

During the Tenth General Assembly of the International Astronomi-
cal Union in Moscow in August, 1958, a symposium was held on the
origin of the earth and planets. This was the first international con-
ference on this subject. Although this symposium was not a part of the
official program of the Assembly, it attracted more than 399 Soviet and
foreign scientists. At the two meetings of the symposium brief papers
were presented by H. Jeffreys (England), G. Kuiper (USA), E. L. Ruskol
(USSR), F. Hoyle (England), A. I. Lebedinskki (USSR), E. Schatzman
(France), B. Yu. Levin (USSR), V. S. Safronov (USSR), H. Urey (USA),
V. A. Krat (USSR) and T. Gold (USA).

Jeffreys discussed certain mainly astronomical difficulties encoun-
tered by the current cosmological hypotheses and stated his opinion
that the formation of the earth's crust presupposes that the earth was
at one time completely molten. In opposing this view, Urey said that
all data point to the formation of the crust as the result of only partial
melting of the earth's mantle.

Kuiper cited a number of arguments which, he believes, show that at
least the giant planets were formed from massive protoplanets of great
size by gradual dissipation of mass. In his first argument he referred
to the chemical composition of the planets, and this brought objections
from the listeners because it is precisely here that Kuiper's hypothesis
encounters difficulties. Kiuper agreed with the criticism contained in

ol's paper and acknowledged that his work on protoplanets requires
_ion.

_yle presented a new variant of the hypothesis of simultaneous
_ation of the sun and the protoplanet cloud. During the formation of
_ in from the contracting nebulosity, when the sun's diameter was
_mes as great as now, a rotational instability caused matter to
_ate from the equatorial zone. It may be supposed that at that
_the sun possessed a considerable magnetic field. Computations
_ that a field of 100 gauss would have been sufficient for the sepa-
_ material to be removed to the limits of the present solar system.
_would have slowed down the rotation of the sun. The gradual cool-
_ the matter moving away from the sun led to the condensation of
_latile elements and compounds at short distances from the sun
_f volatile materials farther away. The terrestrial planets were
_d from accumulations of particles condensed near the sun and the
_planets, from those condensed farther away.

_response to Hoyle's paper, Urey said that, unfortunately, chemical
_ io not substantiate Hoyle's explanation. Gradual cooling of sepa-
_ matter would have led to a very thorough differentiation of it
_ding to the degree of volatility. But the so-called nonvolatile
_rials of the earth include substances of very different degrees of
_lity. For example, mercury is much more volatile than the sili-
_ and should have condensed at a much greater distance from the

_bedinskii suggested that the decrease in the amount of hydrogen
_sing from Jupiter to Saturn is due to the heating of the proto-
_ary cloud caused by the dynamic action of the intermediate bodies
_d within it. The effect of this heating was much greater in the
_ distant planets because of their slower formation.

_vin expressed the idea that although terrestrial planets captured
_ically all solid matter available in their zone, the original amount
_ id matter in the zone of the giant planets was greater than their
_ nt mass. The excess was ejected by the turbulences on these
_ts during the last stages of their formation. Part of the ejected
_r became the gigantic comet cloud (extending for 100,000 astronom-
_nits from the sun) discovered by J. H. Oort.

_e computations of the rate of accumulation of the materials of the
_ cited in Safronov's report show that the formation of the earth was
_ically completed in about 10^8 years. During this time the central
_ of the earth became heated to 1000°C (by radiogenic heat and con-
_on) but the surface always remained cool. The material of the
_ts must have passed through the processes of fragmentation and
_lidation many times, as is indicated by the structure of meteorites.
_ey began his talk by reviewing the data on several elements (Cr,
_ i, Cu, Ga, Zr, In and Pb) whose abundance is different in the sun
_ the meteorites. In some cases the data are not sufficiently exact
_ others this difference is apparently real. Urey has not been able
_ lain this difference by any process of separation of matter during

the formation of the planets and considers it an indication of a different origin of solar and planetary matter. He believes this difference to be a chemical argument in favor of the capture of the protoplanetary cloud by the sun. Urey presented also his computations of the temperature (about 4-6°K), at which a considerable part of hydrogen could have condensed within the protoplanetary cloud assuming that the density of the cloud was equal to Roche density, i.e., was such that the hydrogen could separate in gravitationally stable accumulations. The masses of these condensations, according to the computations, were less than the masses of the existing planets and the total mass of the cloud about 0.35 of the mass of the sun.

Commenting on Urey's report, A. Cameron (Canada) remarked that if the difference in the origin of the solar and planetary materials is manifested in the difference in abundance of elements, it should be manifested also in the difference in their isotopic composition. He expressed doubt in Urey's hypothesis and said that it is necessary to continue the search for the process of separation which must have occurred during one of the stages in the evolution of the protoplanetary cloud.

Krat presented his hypothesis, according to which the giant planets were formed first when the mass of matter was large (and the radiation from the sun great), and the terrestrial planets later.

The second report by Kuiper was devoted to the evolution of the lunar surface and was illustrated with beautiful photographs of the moon. These photographs revealed lunar volcanoes, conical mountains with gentle slopes similar to terrestrial volcanoes (especially submarine). The lunar craters and maria are considered by Kiuper to have been produced by the fall of bodies of various sizes sometimes causing outflows of lava.

Gold spoke on the possibility of formation of the earth's iron core and of its core in the process of gradual heating and partial melting of the earth material. He pointed out that the movement of matter during the stage of gravitational differentiation was very slow and could have occurred everywhere through intercommunicating pores without the formation of large flows.

In conclusion, it should be noted that the majority of the participants in the symposium believe that the planets were formed by gradual accumulation of solid matter. Thus this point of view, developed in our country by O. Yu. Schmidt, is at present the principal approach to the development of planetary cosmology in the whole world.

B. Yu. Levin
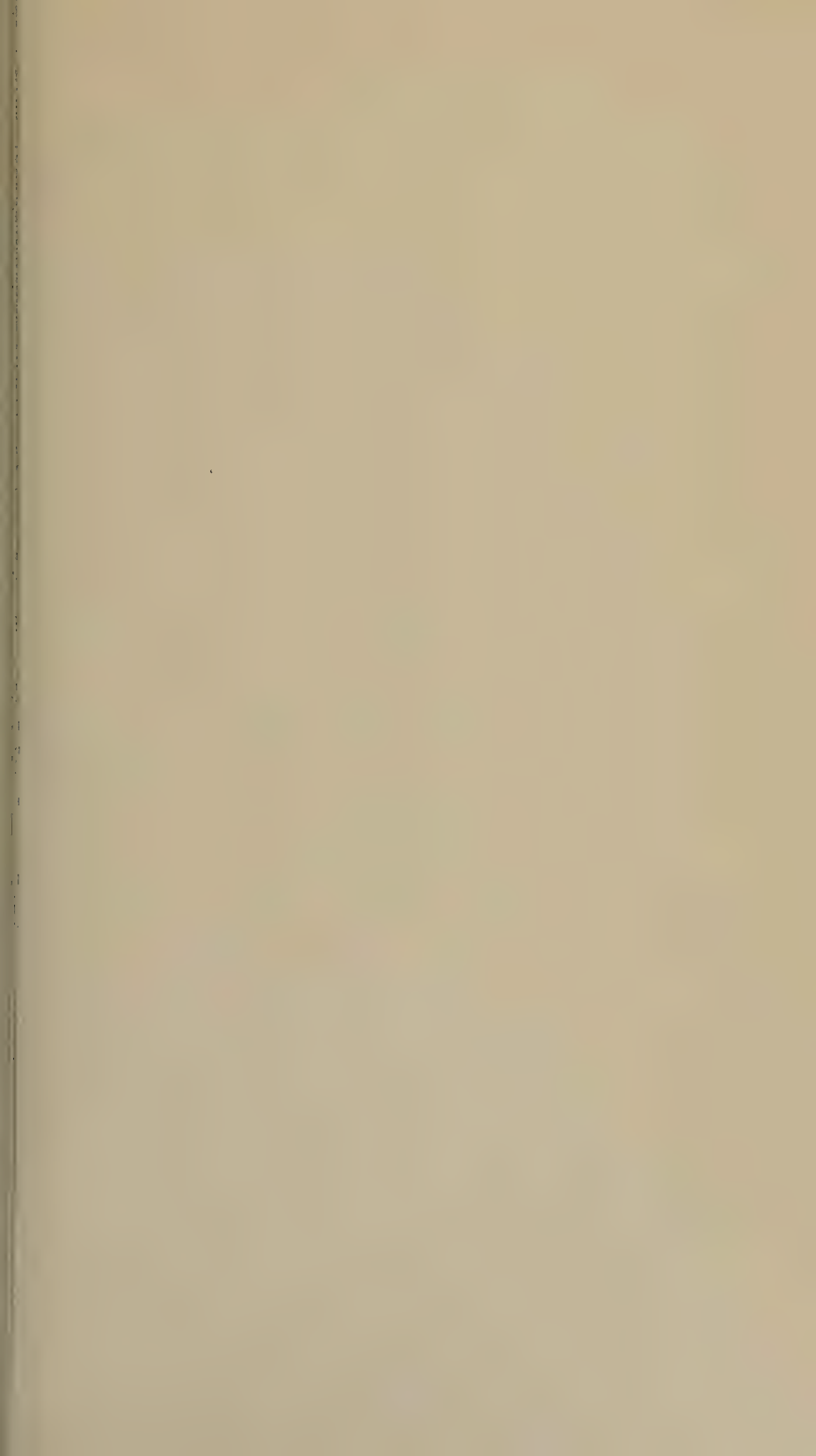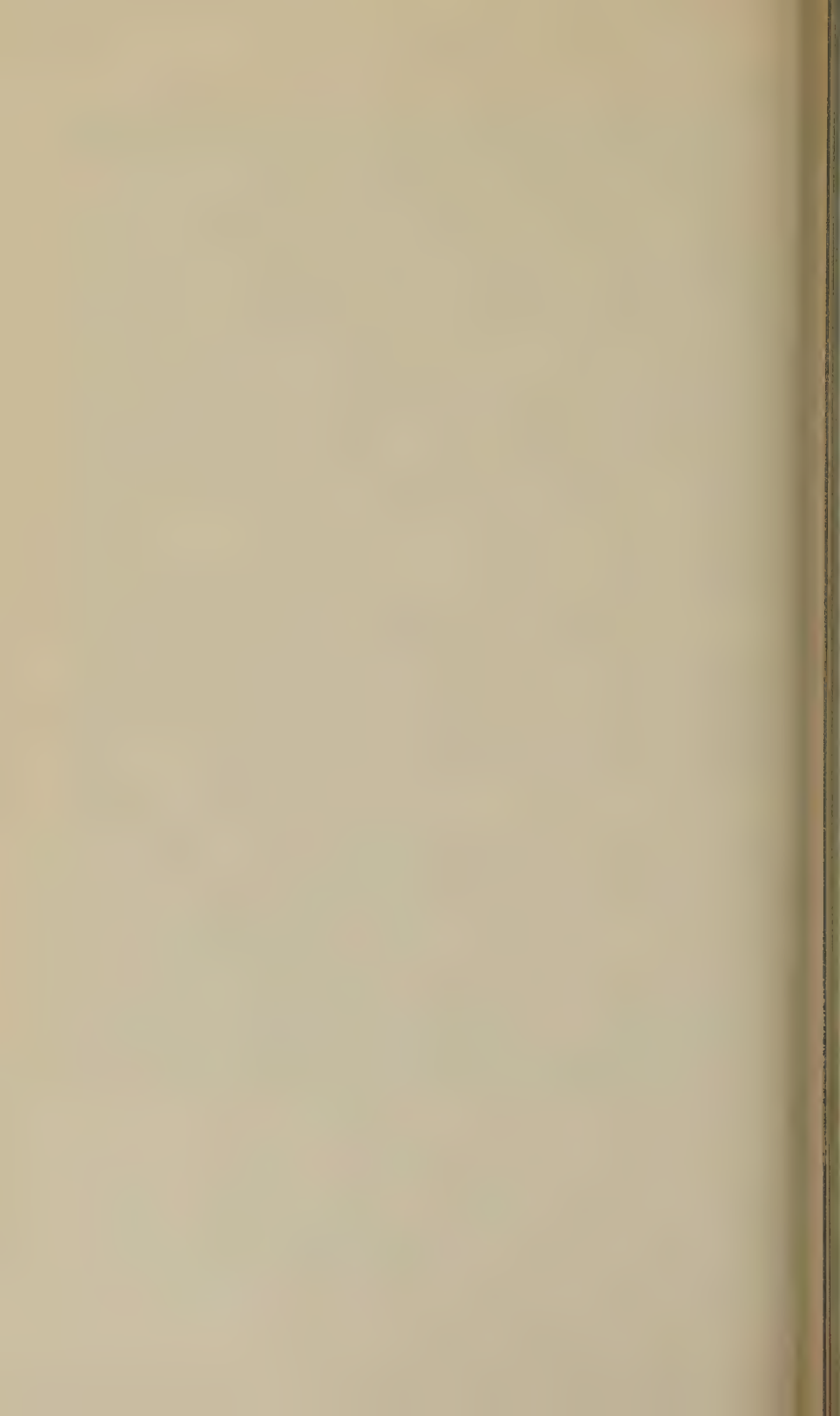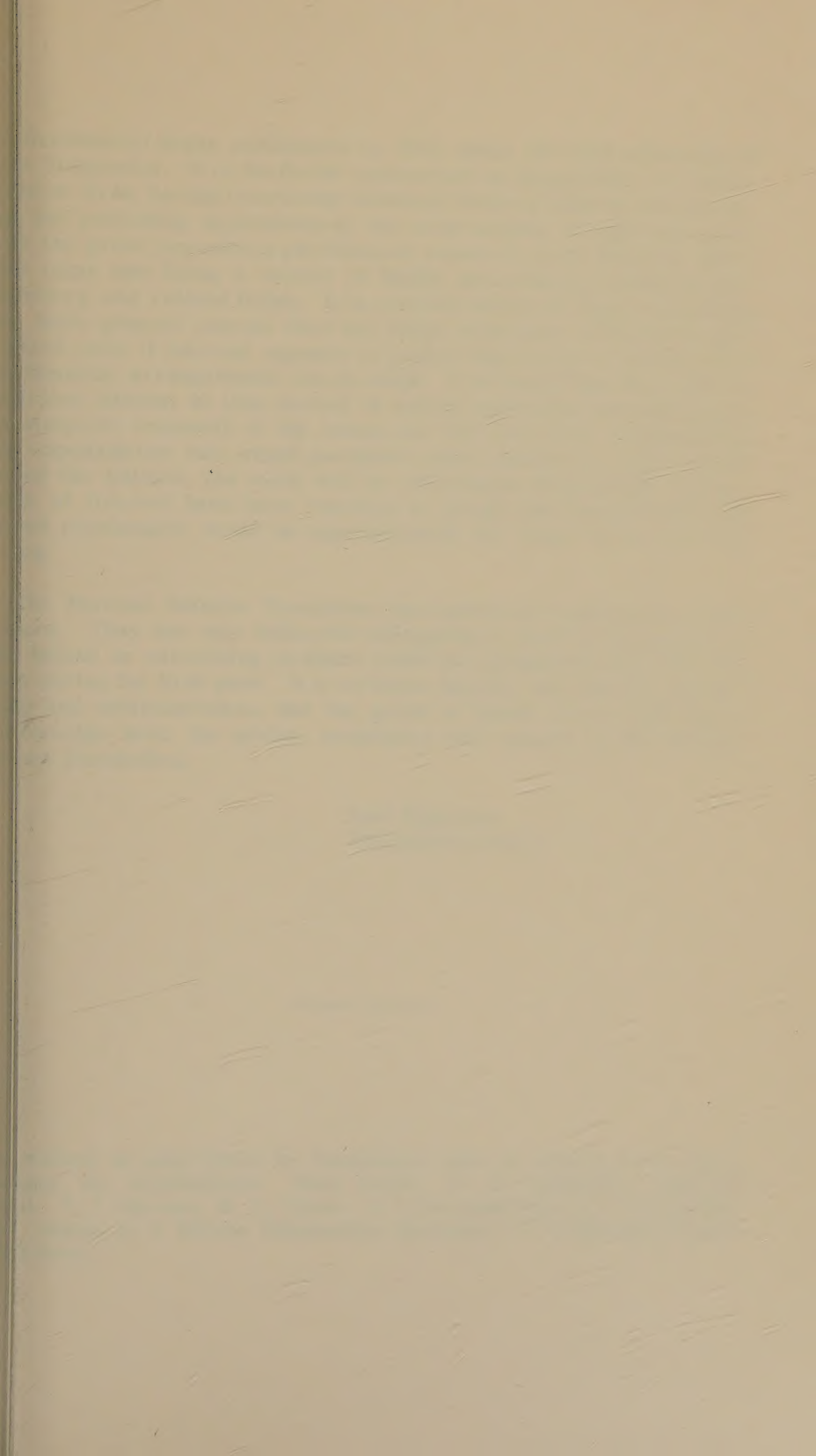
Geokhimiya began publication in 1956 under the able editorship of A. P. Vinogradov. It is the Soviet counterpart of *Geochimica et Cosmochimica Acta,* having practically identical fields of interest and coverage and publishing approximately the same number of pages per year. With the great increase in geochemical research in the U.S.S.R., there have come into being a variety of highly specialized journals in geochemistry and related fields. It is probably better to begin translating the more general journal first and follow with some of the more specialized ones if interest appears to justify this course of action and if the financial arrangements can be made. It is hoped that there will be sufficient interest in this journal to justify translation and publication (complete volumes) of the issues for 1957 and 1956. If individuals or organizations who would purchase such translations will write to one of the Editors, the work will be undertaken when enough expressions of interest have been received to justify the expense involved. Prices presumably would be approximately the same as for the 1958 issues.

The National Science Foundation has been most cooperative in this venture. They not only indicated willingness to back it financially but also helped in calculating probable costs and possible subscription income during the first year. It is on these figures, and those for advertising and administration, that the grant is based. It is a pleasure to acknowledge here the advice, assistance and support of the National Science Foundation.

Earl Ingerson
Translation Editor

Geochemical News is an informal bi-monthly newsletter published by the Geochemical Society and sent without charge to all of its members. It contains news of the activities of the Society, such as summaries of Council Meetings, reports of committees and plans for the future. It also includes announcements of forthcoming meetings and symposia of interest to geochemists, personalia, announcements or short reviews of books of geochemical interest, information on translations and translation services, letters and short notes by members, etc.

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New chemical data and interpretations involving chemical principles are emphasized. For example, papers in chemical mineralogy, petrology, oceanography and volcanology are acceptable, as are those in the chemistry of meteorites, whereas it would be suggested that those in descriptive mineralogy and volcanology, petrography, physical and biological oceanography and physical meteorites, be sent to other journals specializing in these subjects.

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